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THE STRUCTURE OF OPAL AND THE ORIGIN OF ITS IRIDESCENCE

By Sir C. V. Raman and A. Jayaraman

(From the Raman Research Institute, Bangalore)

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1. Introduction

Mineralogists designate as opal a whole group of naturally occurring substances which have silica as their principal chemical constituent, this being usually accompanied by a small but variable percentage of water; they distinguish opal from chalcedony by its lower density. It will be obvious that not all the substances thus designated are necessarily identical in their ultimate physical constitution. The designation of opal is here used in a restricted sense; we are concerned with the species of opal which exhibit certain characteristic optical effects, the origin of which forms the subject of the present paper. Even as thus circumscribed, the category includes substances showing a diversity of optical behaviour. At one extreme, we have the so-called precious opals displaying their characteristic brilliantly coloured internal reflections, and at the other extreme, we have the material known as hyalite which looks very much like ordinary glass. Intermediately, we have other varieties exhibiting distinctive features of their own.

The present investigation was undertaken with the aim of elucidating the origin of the characteristic iridescence of precious opal. Almost inevitably, however, we were led to extend our studies to hyalite and other forms of opal. Our observations showed that the optical behaviour of these materials exhibits certain relationships with each other, indicating certain general structural similarities amongst them. Our X-ray studies have also enabled us to throw some light on the nature of these structures and to put forward an explanation of the iridescence of opal. It may be remarked here that in spite of the great volume of literature which has grown up around the subject, the origin of this well-known phenomenon has so far remained a mystery.

2. Hyalite Exhibiting Diffraction Haloes

The material at our disposal included a piece of transparent hyalite (I). This had been shaped by the lapidary into the form of a thick double-convex

lens with a sharp edge of division between its two surfaces. The diameter of the lens was 11 millimetres and its thickness 6 millimetres. The density of the material was 2·04 and its refractive index as determined by the usual methods was 1·442. Photographs of the specimen (marked as I) are reproduced in Plate IX, Figs. 5 and 6, the illumination being respectively transverse and parallel to the direction of observation.

Seen edgewise in diffuse light, the hyalite exhibited a bluish-white opalescence, but this was not very noticeable when it was viewed normally. If, however, a small bright source of light was viewed *through* the specimen, the image of the source formed by the lens-shaped body was seen to be sorrounded by a diffraction halo exhibiting vivid colours. To elucidate this effect, the specimen was immersed in a flat-sided glass cell containing a mixture of dichloro-ethylene and xylene which was adjusted to have the same refractive index as the hyalite. A bright narrow pencil of light traversed the specimen and after emergence from the cell was received on a viewing screen. Surrounding the central bright spot due to the primary beam appeared a bluish white corona, and beyond this again a brightly coloured diffraction halo. The angular diameter of the halo for red light was 30°. Indications of a second halo appeared further out and clearly separated from the first.

A photograph of the effects described above (marked I) is reproduced in Fig. 1, Plate VI. The area illuminated by the primary beam is heavily overexposed, while *per contra* the exposure was inadequate to record the second outer halo. The first halo is however clearly seen. It is not quite circular but has a hexagonal shape. The photograph was taken with the beam of light passing normally through the lens-shaped hyalite. The general nature of the phenomenon was however not notably influenced by the setting of the piece within the cell.

3. Hyalite Exhibiting Diffraction Spectra

The second specimen (II) which we shall now consider is a material of the same nature as that described in the preceding section, its density being 2·01 and the refractive index 1·441. It had been shaped by the lapidary into a double-convex lens of ellipsoidal form 21 millimetres long, 14 millimetres wide and 9 millimetres thick, a well-defined edge separating its two sides. Under diffuse illumination, the hyalite exhibited a faint milkiness with only a hint of iridescence in its interior. The image of a bright narrow source of light viewed through the piece did *not* exhibit the halo described above for our specimen I. However, in directions inclined at angles ranging from 20° upwards to the direction of the source, brilliant

patches of colour were seen inside the specimen. These became more numerous and vivid as the direction of observation was made more oblique. They reached their maximum brilliancy in directions nearly transverse to the incident light. On the other hand, only vague indications of colour were noticeable in directions lying backwards towards the source.

The significance of the phenomena described above became clear when the specimen was immersed in a flat-sided cell containing liquid, and a brilliant narrow pencil of light sent through it was received on a viewing screen. A whole series of elongated diffraction spectra pointing radially outwards from the direction of the central spot were then seen on the screen, a region surrounding the centre however remaining clear. The spectra appeared over a field of angular radius of 90°. It was, therefore, not possible to photograph the entire group on a single flat plate. The spectra nearest to the direction of the incident beam could, however, be recorded. A photograph thus obtained (marked II) is reproduced in Fig. 1, Plate VI.

The enormous difference in the appearance of the specimen (marked II) when illuminated in directions transverse and parallel to the direction of observation will be evident on a comparison of Figs. 5 and 6 in Plate IX In the former, the whole specimen appears filled with brilliantly coloured patches of light of characteristic shape, while in the latter it appears quite dark.

4. Hyalite Exhibiting Monochromatic Reflections

The third specimen (III) in our collection of which we shall now describe the optical behaviour had a density of 2·03 and a refractive index of 1·442. It had been shaped by the lapidary so that one surface was a highly convex ellipsoid and the other a very flat one, the two being separated by a well-defined edge. The specimen exhibits very beautiful effects when it is illuminated by the light from a brilliant source of small angular extension and is viewed by the observer with the source of light behind him and the specimen held with the highly convex surface facing him. The whole specimen then appears filled inside with brilliant sparkling spangles of colour whose position alters as the specimen is turned round. On the other hand, when a light source is viewed through the specimen, nothing whatever is seen except the transmitted light which is pale yellow in colour. Under diffuse illumination the specimen exhibits a distinct brownish-yellow body-colour which is overlaid by a great number of variously coloured patches of light seen within its volume.

On immersing the specimen in a flat-sided cell containing liquid and sending a narrow pencil of light through it, nothing is seen on the screen

in the forward directions. If, however, a white screen with a hole cut to allow the incident pencil of light to pass through it is placed between the source of light and the cell, the internal reflections by the specimen appear as monochromatic spots of light on the screen. It is not possible to photograph all of them on a flat film owing to the large range of angles involved, and only those appearing in directions nearly opposite to that of the incident beam are recorded. Such a photograph (marked III) is reproduced in Fig. 1, Plate VI. Two photographs of the specimens (marked III) are reproduced in Figs. 5 and 6 of Plate IX. The internal reflections are much more evident in Fig. 5 than in Fig. 6.

A fourth specimen of hyalite (IV) in our collection may also be mentioned here, since we have made use of it in our X-ray studies. It is a small facetted piece shaped by the lapidary into the form of a brilliant with a sharp edge encircling it. The specimen exhibits a very pretty orange-red body colour. It could, however, easily be mistaken for a piece of coloured glass. When immersed in liquid and traversed by a powerful beam of light, one could glimpse patches of internal iridescence. The density of the piece was 2·03 and its refractive index 1·441.

It may be remarked that all the four specimens described above exhibit no noticeable luminescence under ultra-violet illumination.

5. THE X-RAY DIFFRACTION PATTERNS

As already remarked, all the four specimens included in the present study had been shaped into forms having a sharp edge girdling them. It was, therefore, possible to record their X-ray diffraction patterns merely by allowing a fine pencil of X-rays to graze any chosen point on this edge and receiving the diffracted X-rays on a photographic film. The width of the X-ray pencil and its position relative to the edge were adjusted so as to record the pattern with satisfactory definition. The radiation employed was that from a copper target filtered through a nickel foil. The technique employed was tested by using edges of agate; the diffraction rings of cryptocrystalline quartz were then found recorded as sharply defined lines in the correct positions.

The records made with our hyalite specimens using a flat camera are reproduced in Fig. 2, Plate VII, the distance from edge to plate being 4 cm. The patterns recorded with a cylindrical camera of 6 cm. radius are reproduced in Fig. 3, Plate VIII. The numbers entered against each photograph indicate the particular specimen used.

Various authors[1, 2, 3] have claimed that the X-ray pattern of opal is identical with that of high cristobalite. Apart from the difficulty of understanding why the high-temperature form should remain unchanged at the low temperatures, the result reported by those authors leaves the origin of the optical effects displayed by opal unexplained. It seemed to us therefore necessary that a critical comparison should be made of the X-ray patterns of our specimens with those of high and low cristobalite respectively. With this aim and for purposes of comparison with our specimens, we have made use of a porcelain-like material found associated with some specimens of agate collected by one of us near Indore in Central India. The density of this material ranges between 2·30 and 2·35 and its X-ray patterns show it to be low cristobalite mixed with a little tridymite. On heating the material to 300° C., the cristobalite changes reversibly to the high-temperature form, as is shown by its altered X-ray pattern. In Fig. 4, Plate IX the pattern of our hyalite (No. IV) is reproduced in juxtaposition with the patterns of the comparison material recorded at the high and low temperatures respectively.

From a scrutiny of the photographs reproduced in Plates VII, VIII and IX, it is evident that though the X-ray patterns of our specimens exhibit certain similarities with high cristobalite, there are some significant differences demanding attention.

A. The principal ring of hyalite exhibits two components distinctly resolved from each other. This effect is particularly clear in the photographs reproduced in Plate VII. In strongly exposed pictures, the ring exhibits an unsymmetrical broadening.

B. The rings other than the first appearing in the patterns also exhibit large variations in sharpness which are uncorrelated either with the angle of diffraction or with the intensity of the line.

C. Several diffuse bands are present in the patterns of the hyalites which are not seen in the comparison photographs.

6. Interpretation of the Results

The experimental facts set forth above preclude us from describing opal as being merely a cryptocrystalline form of high cristobalite. The doubling of the principal ring indicates, on the other hand, that the material is composite and consists of two distinct phases distributed throughout its volume. A reasonable explanation of the observed features is forthcoming if these two phases are identified respectively with high and low cristobalite. In particular, the doubling of the principal ring appears as an immediate

consequence of the fact that the spacings for high and low cristobalite are different, being 4·11 Å and 4·04 Å respectively.

The lower symmetry of low cristobalite results in its X-ray pattern exhibiting many more spacings than that of high cristobalite.[4, 5, 6] Indeed, while the latter shows only 12 lines with spacings greater than 1 Å, the former shows 43 lines in the same region. Many of the latter lie very close to each other and their intensities are also small. Diffuseness of the rings resulting from the smallness of the crystallites in the material would therefore influence the pattern of low cristobalite with its numerous closely-packed faint lines to a much greater extent than in the case of high cristobalite which has relatively fewer and brighter lines. Indeed, they would in such circumstances, appear in the former case as diffuse bands instead of discrete lines as in the latter case. The presence of low cristobalite in the material would, if the particle sizes are small, thus be readily capable of being overlooked.

7. THE OPTICAL EVIDENCE

The conclusion deduced above from the X-ray data that opal includes two distinct crystalline species of silica in its physical make-up may be also inferred from its optical behaviour.

The optics of stratified media is sufficiently well understood to enable us from a study of the spectral character of the light reflected and transmitted by such a medium, to infer the number and nature of its stratifications. For a high degree of perfection in the monochromatism of the reflections to be possible, it is necessary that the stratifications should be regular in their spacing as well as in their optical character, and further that great numbers of the stratifications should be present. It is also necessary that the reflecting power of an individual stratification is small. For, if the reflecting power of an individual stratification were large, the first few alone of the stratifications would function, and the reflections would necessarily cease to be monochromatic.

It is well-known that the coloured reflections given by precious opal are highly monochromatic and that the light transmitted by them also exhibits monochromatic extinctions. Two further observations that we have made are significant in this connection. In the first place, we have noticed that the internal reflections of opal are perfectly polarised when observed in a direction making an angle of 90° with the incident beam. We have also noticed that a reflection which is highly monochromatic when observed at or near normal incidence retains this character even when it is shifted towards shorter wavelengths by making the incidence oblique.

The optical behaviour of opal thus compels us to recognise the existence of a remarkably perfect periodicity in its structure. It also emerges from the observations that the difference in the refractive indices of the alternate layers is small and yet precisely the same throughout the stratifications. The only reasonable hypothesis that could be put forward to account for these facts is that the alternate layers consist of two distinct and specific modifications of silica.

The conclusions set forth above are supported by the observations described earlier on the optical behaviour of the specimens of hyalite in our collection. Though the individual specimens exhibit distinctive features, it is clear that the phenomena observed have a common origin, namely, the existence of regular optical stratifications within the material; the differences observed arise from the spacing of the stratifications and the dimensions of the individual domains in which they appear not being the same for all the specimens. Thus, hyalite in spite of its apparent dissimilarity in appearance belongs optically to the same category as precious opal.

It may be remarked in conclusion that the density of low cristobalite is 2·32 and its refractive index 1·484, whereas the density of high cristobalite is 2·27 and the refractive index calculated therefrom is 1·468. The difference between the two refractive indices is sufficiently small to be reconcilable with the observed characters of the internal reflections. That the density of our hyalite specimens is distinctly lower than that which might be anticipated on the basis of their structure may be ascribed to the presence in them of ultra-microscopic cavities partly or wholly filled with water. Their existence makes itself evident in a distinct turbidity of the material, a phenomenon which is quite distinct from the optical effects having their origin in the regularly stratified structure of the silica.

8. Summary

A study of the optical behaviour of iridescent opal indicates very clearly that the silica present in the material has a regularly stratified structure in which the alternate layers differ in refractive index, such difference being small but the same throughout the stratifications. A critical examination of the X-ray diffraction patterns of cryptocrystalline hyalites exhibiting optical phenomena identical with or analogous to those of precious opal confirms this finding and enables the two species of silica present in association with each other and giving rise to these phenomena to be identified respectively with high and low cristobalite. The different optical effects exhibited by a stratified medium when the spacing of the stratifications and

the extent of the domains in which they are present are varied have been observed with different specimens of hyalite and are illustrated in the paper by a series of photographs.

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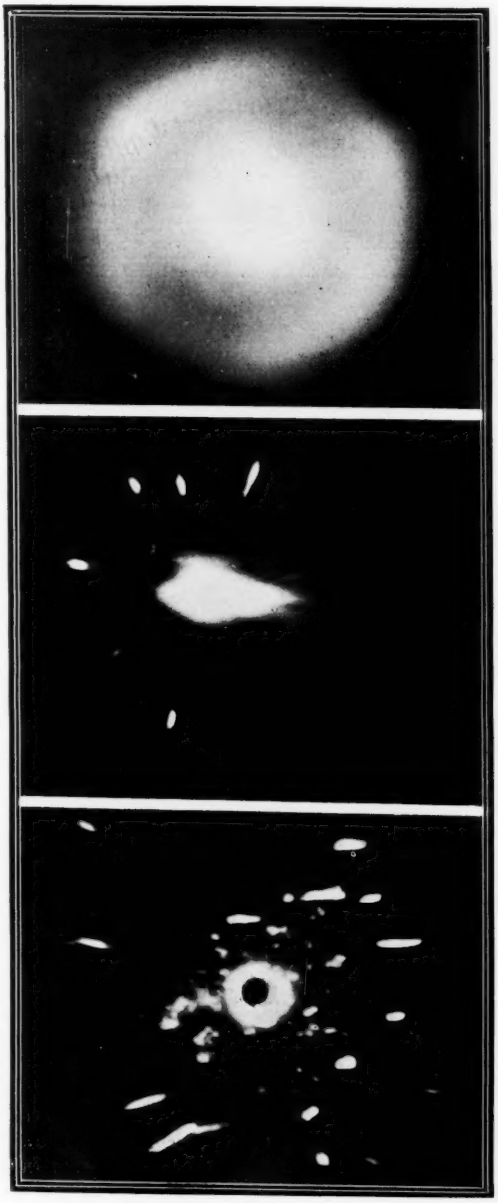

FIG. 1

FIG. 2

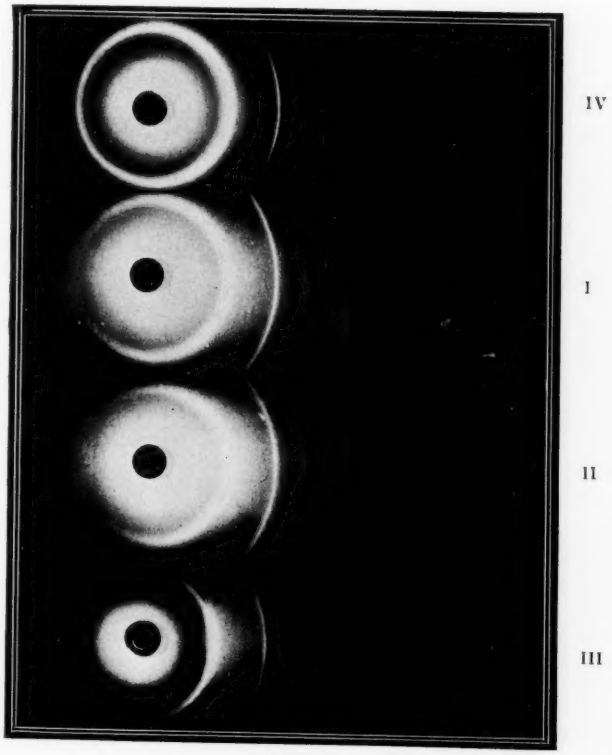

FIG. 3

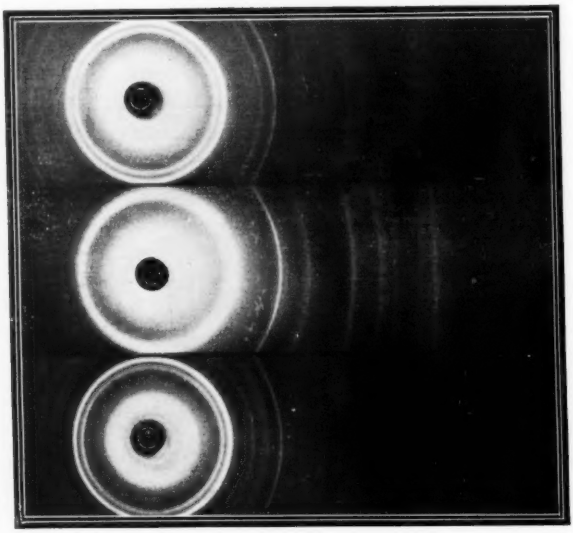

FIG. 4

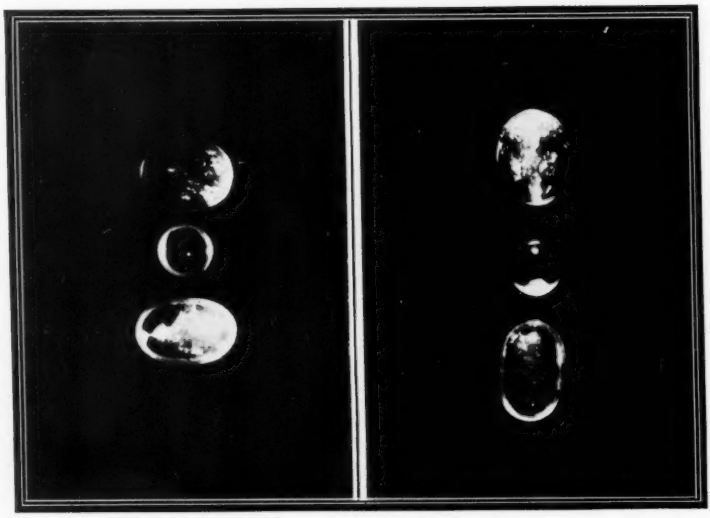

FIG. 5

FIG. 6

MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY IN THE UPPER AIR BY RADIOSONDE

By S. P. Venkiteshwaran, F.A.Sc., B. K. Gupta and B. B. Huddar

(*Poona*)

Received March 28, 1953

The concepts of atmospheric electric phenomena have undergone many changes recently, and as a result there is a trend now to correlate electric to meteorological processes. Measurements have to be made of all the fundamental electric elements, *viz.*, the potential gradient E, the conductivity λ and the vertical air-earth current density i, which are interrelated by Ohm's law, $E\lambda = i$. Investigations of the processes taking place in the atmospheric electric circuit under equilibrium conditions require information about any two of these fundamental quantities, while in other processes all the three quantities must be measured. So far, observations of the potential gradient and conductivity have generally been confined to near the ground, and it has not been possible to extend these observations to the upper air due to the want of a simple technique. There were a few attempts to measure the potential gradient in the atmosphere by radiosonde by Idrac,[1] Ross Gunn[2] and Belin[3] but they did not prove quite satisfactory for general use due to various reasons. But recently Koenigsfeld and Piraux[4] have shown how the simple triode valve HL 23 can be used as an electrometer; they have also shown how this valve electrometer with polonium collectors at a known distance can be coupled to the radiosonde developed in Belgium to measure the electrical potential gradient in the upper air. Venkiteshwaran, Dhar and Huddar[5] have adopted this valve electrometer for use with the audio-frequency modulated American type radiosonde to measure the potential gradient in the atmosphere. This technique has been further simplified by Venkiteshwaran, Gupta and Huddar.[6]

Thus it can be now said that a simple technique for the measurement of the potential gradient in the atmosphere by radiosonde is available due to the valve electrometer of Koenigsfeld and Piraux.

In this paper the attempts made to determine the conductivity of the air at various levels with the valve electrometer are described. Conductivity of the air at various levels have so far been made only with manned

balloons by Wigand,[7] Gish and Sherman[8] during the stratosphere flight of the Explorer II, and more recently by Gish and Wait[9] from aeroplanes. In all these measurements, the Gerdien Condenser[10] has been used.

The Gerdien condenser consists of a central metal cylinder 24 cm. long and 1·4 cm. diameter mounted within a larger cylinder 56 cm. long and 16 cm. in diameter. The inner cylinder is connected to an electroscope and is insulated from the outer. A current of air is drawn through the apparatus by a fan after charging the central cylinder to a known voltage, the outer cylinder being earthed. From the rate of loss of the charge on the central cylinder, the conductivity of the air is calculated. Gerdien deduced the following formula for his apparatus:

$$\frac{C_1}{T} \log_e \frac{V_1}{V_2} = 4\pi\, nev \left\{ \frac{l}{2 \log_e \frac{ra}{ri}} \right\}$$

where C_1 = measured capacity of the central cylinder and electrometer,

V_1 = Potential of the central cylinder at start,

V_2 = Potential of the central cylinder after time T,

T = Time interval in which potential of central cylinder fell from V_1 to V_2,

r_a = Radius of outer cylinder,

r_i = Radius of inner cylinder,

n = Number of ions per c.c. of opposite sign to that given to the central cylinder,

e = Ionic charge,

v = Specific velocity of the ions,

l = Length of the inner cylinder.

From the above formula, the unipolar conductivity nev can be determined. The above formula has been based on the assumption that the force at a distance r from the inner cylinder with a charge E per unit length is $2E/r$ which is not strictly true as the length of the cylinder is short. Swann[11] has suggested the replacement of the factor

$$\frac{l}{2 \log_e \frac{ra}{ri}}$$

by C, the measured value of the capacity of the central cylinder and its connecting rod. Thus we get

$$C_1 \log_e \frac{V_1}{V_2} = 4\pi\, nev\, CT$$

If λ_p and λ_n are the conductivities due to positive and negative ions respectively

$$\lambda_p \text{ or } \lambda_n = \frac{C_1}{4\pi TC} \log_e \frac{V_1}{V_2}$$

the total conductivity being

$$\lambda = \lambda_p + \lambda_n.$$

With the experience gained in the use of the valve electrometer to measure potential gradients, it was felt that it could also be used with the Gerdien condenser to measure the conductivity of the air. The valve electrometer was coupled to the audio frequency modulated type of American radiosonde.

To examine the suitability of the valve electrometer to measure the conductivity of the air, preliminary tests were made on the ground with a Gerdien condenser manufactured by Gunther and Tegetmeyer. Air was drawn through the condenser with a hand-operated fan. The central cylinder was connected to a bifilar Wulf electrometer, also made by Gunther and Tegetmeyer. The rate of fall of potential was first measured with the Wulf electrometer and immediately the observations were repeated with the valve electrometer coupled to the audio frequency modulated radiosonde (Fig. 1). The signals from the radiosonde were recorded in the usual ground equipment

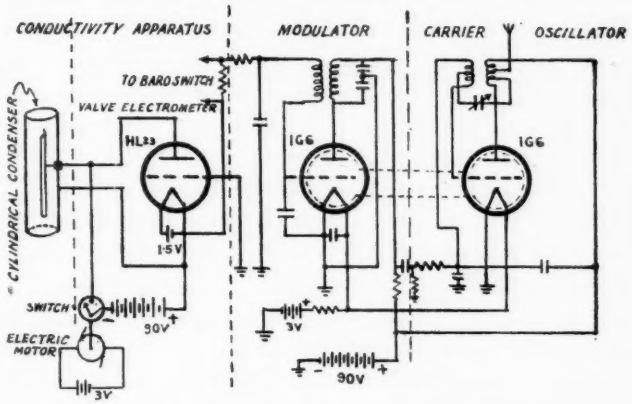

FIG. 1. Gerdien Conductivity Apparatus with Valve Electrometer and American Radiosonde

for the purpose. It was observed that the values of the rate of decrease of voltage of the central cylinder were same.

It was therefore decided to adapt this technique in a suitable and simple manner to measure the conductivity at various levels in the atmosphere.

The outer cylinder of the condenser was made of aluminised paper. It was reinforced with metallic rings at the top and bottom and with strips between the two rings. The dimensions of the cylinder were the same as that in the original Gerdien apparatus. The inner cylinder was made out of an aluminium tube, with its ends closed. It was supported in the centre of the outer cylinder by means of a thin steel wire passing through a piece of alkathene or polysterene insulating piece fixed on the side of the outer cylinder. The inner cylinder was charged to a known voltage (110 volts) at intervals. This was arranged by a battery operated (3 volts) small electric motor (Electrotor, type 240, manufactured by Rev Motors Ltd., Atherstone, Warwickshire, England) and a train of gears operating an alkathene or polysterene cylinder carrying the contracting arms. In one of the ascents the electric motor was replaced by a paper fan similar to that used in the F-type radiosonde.[12]

Before assembling the equipment for ascent the values of C_1 and C were measured in the laboratory. The capacitance of the HL 23 valve was found to vary from valve to valve. The Gerdien cylinder, the radiosonde with the valve electrometer and the switching arrangement to charge the central cylinder were assembled as shown in Fig. 2. The equipment was then calibrated with the radiosonde ground equipment by applying known voltages to the central cylinder, and obtaining a record of the corresponding audio frequency. The equipment was then released with a balloon.

During the flight, the Gerdien condenser is vertically placed and is therefore completely exposed to the vertical air current. The total weight of the equipment is of the order of 2,300 gm. and is lifted with two NR 575 balloons with a total free lift of 5,000 gm. (The Indian NR 575 balloons correspond to Darex 500). The balloons had a rate of ascent of approximately 16 km. per hour. The instrument was hung at a distance of 50 metres from the balloons. Polysterene insulators were employed between the balloons and the instrument.

Fig. 3 shows the records obtained on the 24th February 1953 and 4th March 1953. On the 24th February 1953, the charging of the central cylinder was made with a paper-fan operating during the rise of the balloon. On the 4th March 1953, the charging was effected with an Electrotor motor. On both these days the central cylinder was charged to a negative potential of 110 volts and 115 volts respectively. The conductivity of positive ions calculated from these two ascents is shown in Fig. 4.

Without discussing the details of variation of positive conductivity with height, it is encouraging to note that the values obtained from these ascents

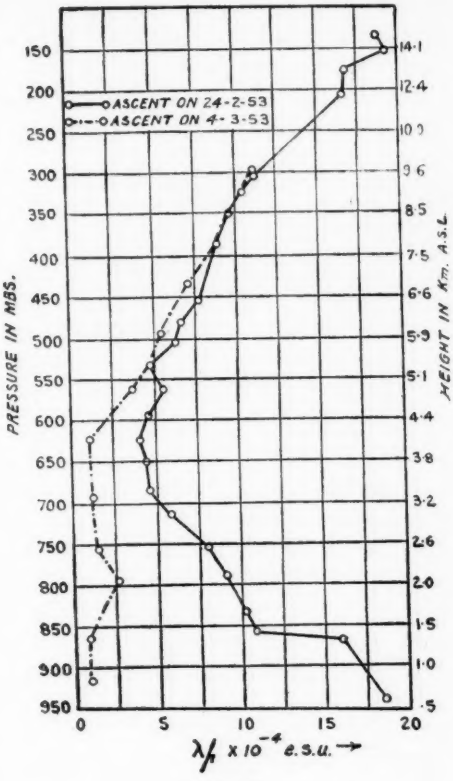

FIG. 4

are comparable with those obtained by Wigand or Gish and Sherman from Explorer II.

When the balloon is released the radiosonde ground equipment records the potential to which the central cylinder is charged and its variation due to leakage due to the positive ions. The baro-switch in the radiosonde also signals the value of the barometric pressure at different heights. One can calculate the conductivity of the air at different levels from the charging potential V_1 supplied by the battery meant for the purpose and V_2, the potential after discharge for a known interval of time measured in the chart. If due to bad reception the charging voltage is missed, the value of V_1 and V_2 can be taken from any points of the trace.

There has been considerable discussion regarding the most suitable voltage to which the central cylinder can be charged. Voltages 115 or 110

have been employed in the two ascents described in this paper. As the ground equipment gives a continuous record of the falling voltage in the central cylinder, any suitable value of V_1 and V_2 can be obtained for the calculation of the conductivity. As the air speed through the condenser is of the order of about 300 metres per minute, it appears that 115 volts is within the "Critical voltage" suggested by Hewlett.[13]

It would have been an improvement in the technique if a suitable funnel was fixed at the upper end of the outer cylinder, to reduce the effects of turbulence and it is hoped that it may be possible to design one in due course.

The technique described in this paper refers only to the measurements of the positive conductivity in the upper air. The method of adapting it to measure the negative conductivity is under examination.

Air conductivity depends upon altitude in a complicated way. Some of the factors that can affect it are:[14] (1) the intensity of cosmic radiation which increases with altitude, (2) for a given ionizing radiation, the rate of ion formation decreases directly as the air density, (3) the mobility of the ions varies inversely as the air density, (4) the rate of ion destruction in pure air of a given ion concentration decreases with altitude, (5) the concentration of radio-active matter exhaled from the earth over land decreases with altitude, and (6) the pollution of the atmosphere decreases with altitude. The last two factors will become insignificant at altitudes greater than one or two kilometres. In addition to the above it is likely that in the troposphere nuclei may tend to gather in layers especially near the boundaries of air masses or in the region of the stratosphere. It appears that the simple technique described in this paper may be useful to throw light on many of the above problems.

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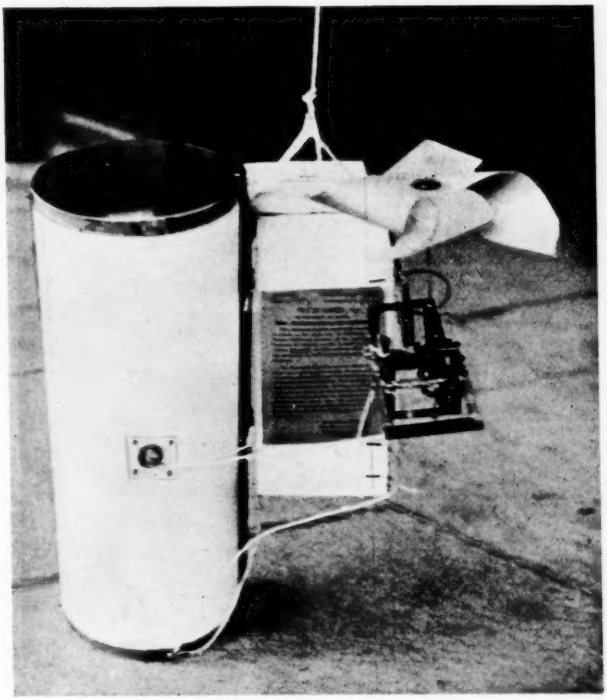

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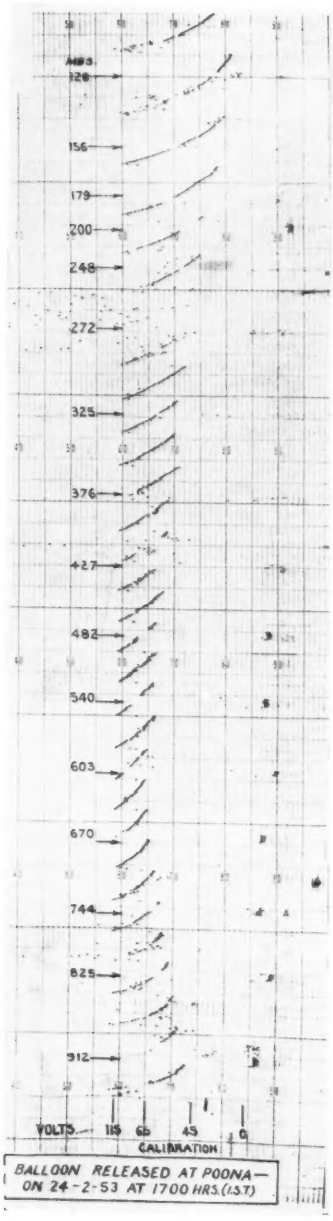
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BALLOON RELEASED AT POONA—
ON 24-2-53 AT 1700 HRS. (I.S.T.)

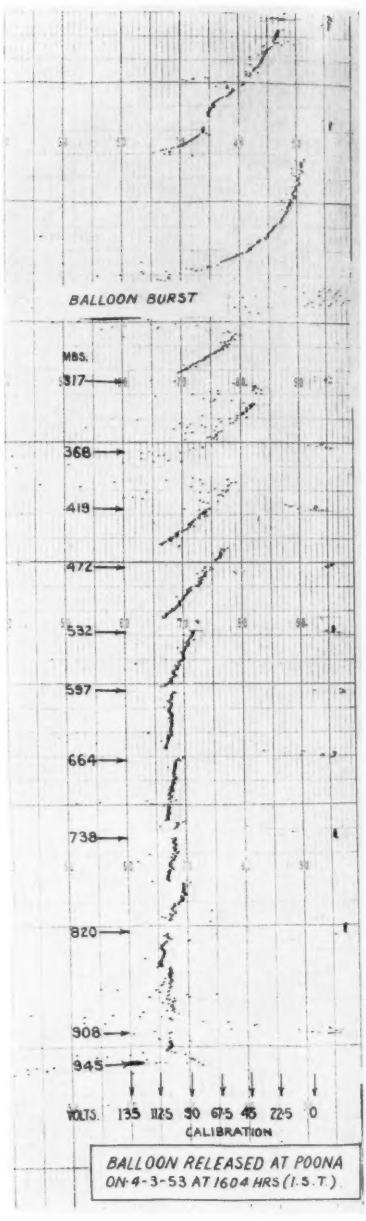
BALLOON BURST
MBS.
317
368
419
472
532
597
664
738
820
908
945
VOLTS. 135 112.5 90 67.5 45 22.5 0
CALIBRATION
BALLOON RELEASED AT POONA
ON 4-3-53 AT 1604 HRS (I.S.T.)

FIG. 3

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THE ROTATION OF AN INFINITE PLANE LAMINA IN A VISCOUS COMPRESSIBLE FLUID

By S. D. Nigam

(Department of Applied Mathematics, Indian Institute of Technology, Kharagpur, India)

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1. Introduction

The steady flow due to the rotation of an infinite plane lamina in an incompressible fluid has been discussed by Th. v. Karman.[1] The corresponding problem in a compressible viscous fluid presents enormous difficulties due to the non-linearity of the equations of motion, viscosity and heat conduction. It has been possible, however, to reduce the equations of motion to three non-linear equations by assuming heat conduction to be negligible and the equation of state to be of the form $p = p_0 + k\rho^\gamma$; p_0, k and γ are constants. The equations have been simplified further by assuming $\gamma = 5/3$ and then integrated after the manner of von Karman.

2. Equations of Motion

The equations of motion for a non-heat conducting viscous compressible fluid, in cylindrical co-ordinates are

$$\rho\left(u\frac{\partial u}{\partial r} + w\frac{\partial u}{\partial z} - \frac{v^2}{r}\right) = -\frac{\partial p}{\partial r} + \frac{\mu}{3}\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(ru) + \frac{\partial w}{\partial z}\right] + \mu\left[\nabla^2 u - \frac{u}{r^2}\right] \quad (1)$$

$$\rho\left(u\frac{\partial v}{\partial r} + w\frac{\partial v}{\partial z} + \frac{uv}{r}\right) = \mu\left[\nabla^2 v - \frac{v}{r^2}\right] \quad (2)$$

$$\rho\left(u\frac{\partial w}{\partial r} + w\frac{\partial w}{\partial z}\right) = -\frac{\partial p}{\partial z} + \frac{\mu}{3}\frac{\partial}{\partial z}\left[\frac{1}{r}\frac{\partial}{\partial r}(ru) + \frac{\partial w}{\partial z}\right] + \mu\nabla^2 w \quad (3)$$

$$\nabla^2 \equiv \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}$$

and the equation of continuity is

$$\frac{1}{r}\frac{\partial}{\partial r}(ru\rho) + \frac{\partial}{\partial z}(w\rho) = 0, \quad (4)$$

where u, v, w are the radial, the azimuthal and the axial components of velocity respectively. If the lamina rotates with an angular velocity Ω about an axis perpendicular to its plane, we put

$$u = \Omega r f(z_1)\ ;\quad v = \Omega r g(z_1)\ ;\quad w = (\mu\Omega)^{\frac{1}{2}} h(z_1);\quad p = p_0 - \mu\Omega p_1(z_1)$$

$$z_1 = (\Omega/\mu)^{\frac{1}{2}} z$$

and obtain the following equations:

$$\rho\,[f^2 - g^2 + f'h] = f'' \tag{5}$$

$$\rho\,[2fg + g'h] = g'' \tag{6}$$

$$\rho h h' = p_1' + (2/3)\,(f' + 2h'') \tag{7}$$

$$2f\rho + \frac{d}{dz_1}(h\rho) = 0 \tag{8}$$

where a dash denotes differentiation with respect to z_1. We further assume, $\rho = -h^3(z_1)$. The equation for pressure using (8) becomes

$$p_1' = -h^4 h' \text{ or } p_1 = (1/5)\,\rho^{5/3}.$$

Therefore,* $$p = p_0 - (\mu\Omega/5)\,\rho^{5/3}. \tag{9}$$

Equations (5), (6) and (8) become

$$h^3\,[f^2 - g^2 + f'h] + f'' = 0 \tag{10}$$

$$h^3\,[2fg + g'h] + g'' = 0 \tag{11}$$

$$f + 2h' = 0 \tag{12}$$

The solutions of these equations have to satisfy the following boundary conditions:

$$f(0) = f(\infty) = 0;\quad g(0) = 1,\ g(\infty) = 0;\quad h(0) = 0 \tag{12 a}$$

For small values of z_1, we have

$$f = a_0 z_1 - \frac{a_0^3}{3584} z_1^8 - \frac{a_0^3 b_0}{2304} z_1^9 + \frac{a_0^3\,(3a_0^2 - 4\,b_0^2)}{23040} z_1^{10} + \ldots. \tag{13}$$

$$g = 1 + b_0 z_1 + \frac{a_0^4}{2304} z_1^9 + \frac{7 a_0^4 b_0}{23040} z_1^{10} + \ldots. \tag{14}$$

$$h = -\frac{a_0}{4} z_1^2 + \frac{a_0^3}{64512} z_1^9 + \frac{a_0^3 b_0}{46080} z_1^{10} + \ldots. \tag{15}$$

For large values of z_1, we have

$$f = \mathrm{A} e^{-c z_1} - \frac{\mathrm{A}^2 + \mathrm{B}^2}{2cc_0} e^{-2c z_1} + \ldots. \tag{16}$$

$$g = \mathrm{B} e^{-c z_1} + \ldots. \tag{17}$$

* On account of the boundary conditions (12 *a*) the density becomes zero on the rotating lamina. This has been pointed out earlier by Lord Kelvin. [*Papers*, **1**, 83–87]. Also ref. C. Truesdell, *On the Equation of the Bounding Surface*, Publication, U. S. Naval Research Laboratory, 1951, 71–78.

$$h = -c_0 + \frac{A}{2c} e^{-cz_1} - \frac{A^2 + B^2}{8c^2 c_0} e^{-2cz_1} + \ldots; \quad c_0^4 = c \tag{18}$$

The constants a_0, b_0, c, A and B have to be chosen so that f, g, h, f' and g' are continuous for some finite value of z_1 and it will then follow from the differential equations that all other derivatives are continuous.

3. Determination of Constants

We follow a method of approximation to determine the coefficients. It is highly probable that the expressions (13), (14) and (15) are convergent for $z_1 \leqslant 1$. The coefficients of various terms are decreasing rather rapidly, so that, even for $z_1 = 1$ we neglect terms $\sim O(z_1^8)$. Again, in (16), (17) and (18) we neglect terms $\sim O(e^{-3cz_1}.)$ The equations for constants are

$$a_0 = Ae^{-c} - \frac{A^2 + B^2}{2cc_0} e^{-2c}$$

$$1 + b_0 = Be^{-c}$$

$$-\frac{a_0}{4} = -c_0 + \frac{A}{2c} e^{-c} - \frac{A^2 + B^2}{8c^2 c_0} e^{-2c}$$

$$a_0 = -c\left[Ae^{-c} - \frac{A^2 + B^2}{cc_0} e^{-2c}\right]$$

$$b_0 = -c\, Be^{-c}.$$

The constants are

$$a_0 = 3{\cdot}634,\ b_0 = -{\cdot}833,\ c = 5,\ c_0 = 1{\cdot}49,\ A = 1184{\cdot}232,\ B = 24{\cdot}735.$$

The functions f, g, h, are given in Fig. 1.

f and g tend to zero exponentially and become indistinguishable from zero for $z_1 = 2$. Hence, if, μ/Ω is small, $\mu/\Omega r$ and $v/\Omega r$ are appreciable only in a thin layer $[\delta = (\mu/\Omega)^{\frac{1}{2}} \cdot 2]$ near the disk. This points to the existence of a boundary layer adjacent to the rotating lamina.

The solution applies strictly only to an infinite disc; but if we neglect the edge effect we can find the frictional moment on a rotating disk of radius a. The shearing stress is given by

$$p_{z\phi} = \mu \frac{\partial v}{\partial z} = (\mu\Omega^3)^{\frac{1}{2}} rg'(0) \ldots\ldots \text{ at the disk, so that the moment is}$$

$$M = -\int_0^a 2\pi r^2 p_{z\phi} dr = \pi a^4 (\mu\Omega^3)^{\frac{1}{2}} \times {\cdot}4165.$$

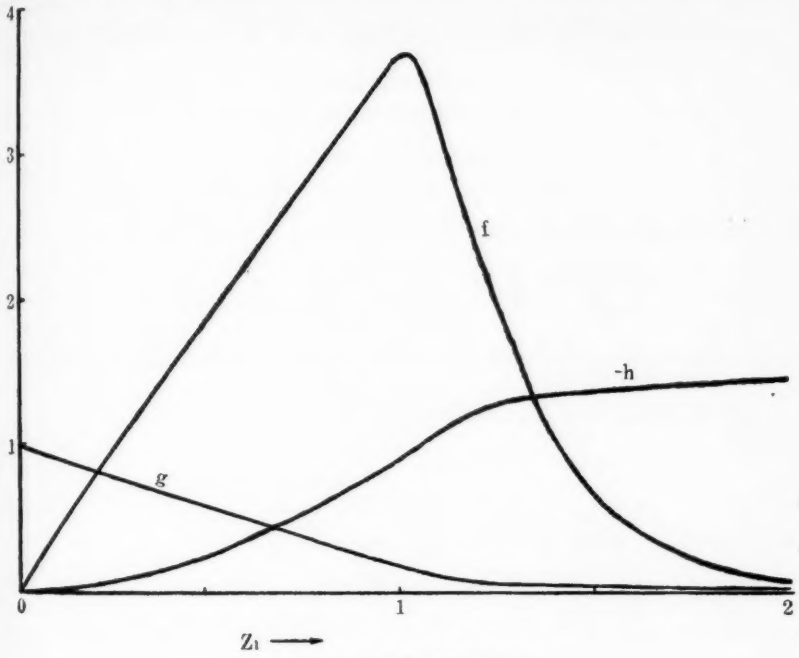

FIG. 1 The flow functions

4. SUMMARY AND DISCUSSION OF RESULTS

In the corresponding problem for the incompressible viscous fluid[2] the functions mod. f and mod. h are everywhere less than the maximum value of mod. g. In our case the functions mod. f and mod. h are at some places greater than the maximum value of mod. g. The radial and the axial components of velocity at some places exceed the velocity of the disc. This is quite in accord with the phenomena associated with the compressibility of the fluids. But for these compressibility effects, which are confined to the neighbourhood of the disc, the general features of flow are same as in incompressible fluids. There is a steady axial flow towards the rotating lamina; this is necessary to preserve continuity. The fluid moves radially outwards near the lamina.

In conclusion, I thank Mr. K. S. Rangasami and Mr. R. S. Gupta for the help they have given me in checking up the numerical results and in drawing the sketches.

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A NOTE ON A PAPER OF R. C. BUCK

BY S. K. SINGH

[*D. S. College, Aligarh (India)*]

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LET $f(z)$ be an entire function of order $\rho\ (0 < \rho < \infty)$ and let

$$\limsup_{\inf.}{}_{r\to\infty} \frac{\log M(r)}{r^\rho} = \frac{T}{t}, \quad \limsup_{\inf.}{}_{r\to\infty} \frac{n(r)}{r^\rho} = \frac{L}{l},$$

where $M(r)$ is $\underset{|z|=r}{\text{Max}} |f(z)|$ and $n(r)$ is the number of zeros of $f(z)$ in $|z| \leqslant r$.

(R. P. Boas, 1946) has proved that

$$l \leqslant \rho T \tag{1}$$

and

$$L \leqslant e\rho T \tag{2}$$

Recently (R. C. Buck, 1952) has proved that

$$l + eL \leqslant e^2\rho T \tag{3}$$

and with the help of (3) he proved that equality cannot hold simultaneously in (1) and (2). He further proves that if

$$l = \rho T \tag{4}$$

then

$$L \leqslant (2\cdot 32\ldots.)\,\rho T \tag{5}$$

The purpose of this note is to see how far Buck's results can be improved. (S. M. Shah, 1948, lemma 2·1) has already proved an inequality better than (3), namely

$$L + l \leqslant e\rho T \tag{6}$$

From (6) it is clear that if $L = e\rho T$, then $l = 0$. We prove:

THEOREM.—(i) If (4) holds then

$$L = \rho T$$

(ii) and that equality cannot hold simultaneously in (1) and (6) and hence *a fortiori* it can not hold simultaneously in (1) and (2) too.

Proof.—(i) If $l = \rho T$, then clearly $L \geqslant \rho T$, hence it is sufficient to prove that $L \leqslant \rho T$.

Now $n(r) > (l - \epsilon)\, r^\rho$ for $r \geqslant r_0 = r_0(\epsilon)$.

Let $k \geqslant 1$ then

$$\int_0^{rk^{1/\rho}} \frac{n(t)}{t}\, dt \leqslant A + \log M(rk^{1/\rho})$$

hence

$$\int_0^{r_0} + \int_{r_0}^{r} + \int_{r}^{rk^{1/\rho}} \leqslant A + \log M(rk^{1/\rho})$$

so

$$\frac{(l-\epsilon)\, r^\rho}{\rho} + n(r) \int_r^{rk^{1/\rho}} \frac{1}{t}\, dt \leqslant A_1 + \log M(rk^{1/\rho})$$

hence

$$\frac{(l-\epsilon)\, r^\rho}{r^\rho k^\rho} + \frac{n(r) \log k}{\rho r^\rho k} \leqslant o(1) + \frac{\log M(rk^{1/\rho})}{r^\rho k}$$

hence

$$\frac{l}{k\rho} + \frac{L \log k}{k\rho} \leqslant T$$

so

$$L \leqslant \frac{T\rho\,(k-1)}{\log k}$$

Put $k = 1 + \eta$, where η is a positive quantity tending to zero.

Then

$$L \leqslant T\rho \frac{\eta}{\eta + O(\eta^2)}$$

hence

$$L \leqslant \rho T$$

Proof.—(ii) Let $l = \rho T$, then by the above

$$L = \rho T$$

so

$$l + L = 2\rho T < e\rho T.$$

Now let $l + L = \rho e T$, then l will be less than ρT for if it were equal to ρT then $l + L$ will have to be less than $e\rho T$.

Finally, I thank Dr. S. M. Shah for suggesting the problem to me and helping me throughout the preparation of this paper.

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SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XXXIII. Synthesis of Isodaidzein and Its Methyl Ethers

BY P. K. GROVER AND T. R. SESHADRI, F.A.SC.

(From the Department of Chemistry, University of Delhi, Delhi)

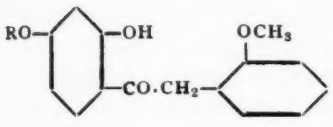
Received March 17, 1953

OKANO AND BEPPU[1] reported that two of the crystalline components of soya beans were 2′-hydroxy isoflavone derivatives (isogenistin and 8-methyl isogenistin). Recent synthetic work[2–5] has proved that the structures assigned to the natural products are incorrect. However, the degradation reactions of Okano and Beppu show that 2′-hydroxy isoflavone structures are present in the naturally occurring compounds. Pterocarpin and homopterocarpin definitely contain 2′-hydroxy isoflavan structures[6] and rotenone and allied chromano-chromanones may be considered to be derived from 2′-hydroxy isoflavanones.[7] Ferreirin and homoferreirin have recently been given the constitution of isoflavanones of this type.[17] Though the occurrence of the simple isoflavanone nucleus in nature was reported first in the case of padmakastein (Narasimhachari and Seshadri[18]), ferreirin and homoferreirin are representatives of isoflavanones having a hydroxyl or methoxyl group in the 2′-position. Therefore it is reasonable to expect that simpler members of this type such as 7 : 2′-dihydroxy isoflavone (isodaidzein) (II *a*) may occur in nature. Representatives having a hydroxyl group in the 2′-position are found in the related group of flavonols, *e.g.*, morin,[8] datiscetin.[9] Further, certain special features appeared to exist in the demethylation of 2′-methoxy isoflavones.[2, 4, 5] The 2′-hydroxyl group in isoflavones seems to be somewhat resistant to methylation and differs from the 4′-hydroxyl group in this respect.[7] In order to study more fully these points, a synthesis of isodaidzein (II *a*) has now been undertaken.

Partial methylation of 2 : 4-dihydroxy-2′-methoxy phenyl benzyl ketone (I *a*)[7] gives rise to its 4-O-methyl ether (I *b*). Treatment of this ketone with ethyl formate and sodium at 0°,[10] yields 7 : 2′-dimethoxy isoflavone (II *b*). The ketone (I *b*) seems to be rather unreactive in this reaction and in several experiments, it is recovered unchanged. The exact conditions which would consistently lead to the formation of the isoflavone could not be determined. Another point is noteworthy. The related ketones, 2-hydroxy-4 : 6 : 2′-trimethoxy phenyl benzyl ketone[4] and 2-hydroxy-3-methyl-4 ; 6 : 2′-trimethoxy

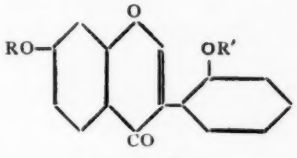
phenyl benzyl ketone[5] on treatment with ethyl formate and sodium yield 2-hydroxy isoflavanones which could be converted into the isoflavones subsequently.[11] However in the present case, the ketone (I *b*) does not yield a 2-hydroxy isoflavanone but only the isoflavone (II *b*). The formation of 2-hydroxy isoflavanones in ethyl formate condensations therefore is not a characteristic property of 2′-methoxy phenyl benzyl ketones (see also Späth and Schläger[12]).

Demethylation of the isoflavone (II *b*) with hydriodic acid furnished isodaidzein (II *a*) in a poor yield. The difficulties of demethylation of such 2′-methoxy isoflavones with hydriodic acid or hydrobromic acid seem to be characteristic of these compounds. However by employing aluminium chloride in benzene solution,[13] a good yield of isodaidzein is obtained. It does not give any colour with alcoholic ferric chloride showing that the 2′-hydroxyl group does not form part of any chelate structure. Its diacetate has also been prepared.



(I)

a, R = H
b, R = CH_2



(II)

a, R = R′ = H
b, R = R′ = CH_3
c, R = H, R′ = CH_3
d, R = CH_3, R′ = H

Formononetin[14] is the naturally occurring 4′-methyl ether of daidzein and similarly partial methyl ethers of isodaidzein may also be expected to occur in nature and these have now been prepared. Condensation of the ketone (I *a*) with ethyl formate and sodium gives rise to the isoflavone (I *c*). It is purified through its acetate. The preparation of this partial methyl ether (I *c*) from the dihydroxy ketone (I *a*) is analogous to the synthesis of formononetin itself which has been reported earlier.[15] This is another example to show that the protection of the hydroxyl group at the 4-position in the ketone of type (I *a*) before isoflavone condensation is not essential.

Treatment of isodaidzein (II *a*) with excess of methyl iodide and potassium carbonate in acetone solution furnishes predominantly the 7-methyl ether (II *d*). The behaviour of isodaidzein in this reaction is similar to that of its 2-methyl derivative, already recorded[7] and this shows that the hindrance to the methylation of the 2′-hydroxyl group is not due to the 2-methyl group. The negative ferric reaction in the case of isodaidzein

indicates the absence of chelation with the carbonyl of the pyrone ring and therefore the resistance of the 2′-hydroxyl group to methylation seems to be due to other factors. This partial methylation is the only convenient procedure for obtaining the 7-monomethyl ether (II *d*) since partial demethylation with acids, which has been so successful in other cases[15, 16] does not proceed well in the present case.

EXPERIMENTAL

2-Hydroxy-4: 2′-dimethoxy phenyl benzyl ketone (I b)

To a solution of 2: 4-dihydroxy-2′-methoxy phenyl benzyl ketone (2·5 g.) in dry acetone (100 c.c.), dimethyl sulphate (1·05 c.c.) and anhydrous potassium carbonate (3 g.) were added and the mixture refluxed for 5 hours. The acetone solution was filtered off and the potassium salts were washed with acetone. The solvent was distilled off from the filtrate. Addition of petroleum ether to the residual oil yielded a crystalline solid. This was filtered and recrystallised from alcohol. 2-Hydroxy-4: 2′-dimethoxy phenyl benzyl ketone separated as thick colourless prisms melting at 93–94°. Yield 2·2 g. It gave a deep pink colour with alcoholic ferric chloride and was easily soluble in 10% aqueous sodium hydroxide (Found: C, 71·0; H, 6·0; $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

7: 2′-Dimethoxy isoflavone (II b)

A solution of the ketone (1 g.) in freshly distilled ethyl formate (15 c.c.) was added to powdered sodium at 0°, gradually with shaking in the course of 30 minutes. The mixture was left in the refrigerator for 48 hours. Pieces of ice were added and after allowing the ethyl formate to evaporate, the mixture was extracted with ether. The ether solution was washed with aqueous sodium hydroxide (10%) to remove unchanged ketone and then with water and finally evaporated. The residue, when crystallised twice from alcohol, yielded 7: 2′-dimethoxy isoflavone as colourless rectangular rods melting at 111–12°. The yield varied considerably and in many condensations, most of the ketone was recovered. The maximum yield obtained in any experiment was about 55% (Found: C, 72·3; H, 5·3; $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%).

7: 2′-Dihydroxy isoflavone (Isodaidzein) (II a)

(i) To a solution of the above dimethoxy isoflavone (0·8 g.) in acetic anhydride (14 c.c.) was added hydriodic acid (20 c.c.) and the mixture heated in an oil-bath at 140–50° for 2 hours. It was cooled and diluted with saturated aqueous sodium bisulphite (60 c.c.). The dark solid that

separated overnight was filtered and crystallised from dilute alcohol (Norit) twice, when 7:2′-dihydroxy isoflavone separated as thick colourless long rectangular prisms melting at 208–9°. Yield 60 mg. It was easily soluble in alcohol and dilute aqueous sodium carbonate and it did not give any colour with ferric chloride in alcoholic solution (Found: C, 71·0; H, 4·1; $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%).

(ii) 7:2′-Dimethoxy isoflavone (0·45 g.) was dissolved in dry benzene (30 c.c.) and powdered anhydrous aluminium chloride (1·3 g.) added. The mixture was refluxed for 2 hours in a water-bath. Benzene was then distilled off and the aluminium chloride complex decomposed by the addition of ice and hydrochloric acid (10 c.c.). The grey solid that was obtained was filtered after 8 hours and was repeatedly macerated with aqueous sodium carbonate (10%). A small amount of insoluble matter was filtered off. The filtrate on acidification yielded a colourless solid which when crystallised from dilute alcohol gave 7:2′-dihydroxy isoflavone as colourless rectangular prisms melting at 208–9° alone or when mixed with a sample described in (i) above. Yield 0·2 g.

The diacetate, prepared by acetylation with acetic anhydride and pyridine, crystallised from alcohol as colourless thick rectangular tablets melting at 144–45°. It was easily soluble in hot alcohol (Found: C, 67·7; H, 4·4; $C_{19}H_{14}O_6$ requires C, 67·5; H, 4·1%).

7-Hydroxy-2′-methoxy isoflavone (*II c*)

A solution of 2:4-dihydroxy-2′-methoxy phenyl benzyl ketone (1·3 g.) in ethyl formate (20 c.c.) was added to powdered sodium (1 g.) at 0° and kept for 48 hours at the same temperature. Ice and hydrochloric acid were then added, the unreacted ethyl formate was evaporated off and the pale yellow solid filtered and washed with water. It melted at about 165° and gave a positive ferric reaction and was therefore a mixture of the unchanged ketone and the isoflavone. The pure isoflavone could not be obtained by crystallisation and the mixture was therefore acetylated with acetic anhydride and pyridine. The product when crystallised twice from alcohol yielded 7-acetoxy-2′-methoxy isoflavone as long thin colourless rectangular plates tapering at one end and melting at 137–39° (Found: C, 69·3; H, 4·2; $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·5%).

The above acetate (0·15 g.) was dissolved in a mixture of alcohol (8 c.c.) and concentrated hydrochloric acid (8 c.c.) and the solution boiled in a water-bath for 15 minutes. It was diluted with water and the alcohol distilled off. The colourless crystals that separated on cooling were collected and recrystallised from alcohol twice when 7-hydroxy-2′-methoxy

isoflavone was obtained in the form of sheaves of colourless plates melting at 230–32°. It was soluble in dilute aqueous sodium carbonate and did not give any colour with alcoholic ferric chloride (Found: C, 71·6; H, 4·9; $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

Methylation of 7: 2'-dihydroxy isoflavone (II a)

7: 2'-Dihydroxy isoflavone (0·7 g.) was dissolved in acetone (100 c.c.) and the solution refluxed with methyl iodide (4 c.c.) and potassium carbonate (5 g.) for 3 hours on a water-bath. The acetone solution was filtered and the potassium salts were washed with warm acetone. The residue left on distilling off the solvent from the combined filtrate was taken up in ether. The ether solution was extracted with aqueous sodium hydroxide (10%) thrice. The precipitate obtained on acidification of the alkaline solution was filtered and crystallised twice from alcohol, when 7-methoxy-2'-hydroxy isoflavone (II *d*) separated as stout colourless rectangular prisms melting at 148°. Yield 0·4 g. (Found: C, 71·7; H, 4·6; $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). The acetate, prepared by the acetic anhydride-pyridine method, crystallised from alcohol as colourless plates and prisms melting at 134-35° (Found: C, 70·0; H, 4·2; $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·5%).

The original ether solution left after extraction with alkali was washed with water and evaporated. The residue crystallised from alcohol as colourless rectangular rods melting at 111–12° alone or when mixed with a sample of 7: 2'-dimethoxy isoflavone (II *b*) described earlier. Yield 30 mg.

SUMMARY

The synthesis of isodaidzein and of its methyl ethers has been carried out and their properties studied. The special features noticed earlier in the case 2'-hydroxy isoflavones are also found here and they seem to be characteristic of the presence of the 2'-methoxy and hydroxy groups in isoflavones.

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PETROSELINIC ACID: OCCURRENCE IN SOME UMBELLIFERÆ SEED FATS

By K. N. Menon, F.A.Sc. and P. S. Raman

(Maharaja's College, Ernakulam and Madras University Laboratory, Guindy)

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The umbelliferæ seed fats are characterised by the presence of Δ^6-octadecenoic acid or petroselinic acid as the chief component fatty acid. Its lead salt is sparingly soluble in cold alcohol, by reason of which it is separated from oleic and linoleic acids, the other unsaturated acids usually present in these fats.

The present investigation deals with the examination of seed fats derived from three typical members of the umbelliferæ, much grown in India, *viz.*, *Cuminum cyminum* (Cumin), *Anethum sowa* (Dill) and *Ptychotis Ajowan* (Ajowan). Grimme,[1] who isolated these fats, reports only on some of the constants. A detailed analysis of the fatty acids has shown that petroselinic acid is present to the extent of 21, 45 and 42% respectively of the total fatty acids in these three seed fats. Cumin seed fat is exceptional by the presence of stearic and arachidic acids, in addition to palmitic acid, the only saturated acid usually present in umbelliferæ seed fats.

The identity of petroselinic acid was proved by first obtaining 6:7-dihydroxy stearic acid by alkaline permanganate oxidation and then oxidising the dihydroxy acid with lead tetracetate yielding adipic semialdehyde, lauric aldehyde and the corresponding acids. Oxidation with peracetic and performic acids gave the lower melting dihydroxy-acid of m.p. 117°. The *trans*-acid, formed from the *cis*-acid with nitrous acid gave, on the other hand, the higher melting dihydroxy acid of m.p. 122°. Instead of the usual hydrogen peroxide-organic acid mixture, a modified procedure involving a mixture of barium peroxide-sulphuric acid-organic acid, was employed with good results. These oxidation products are exactly the reverse of those obtained by alkaline permanganate oxidations, wherein the *cis*-acid gives a product melting at 122° and the *trans*-acid a product melting at 117°. These results involving an inversion with alkaline permanganate are in full agreement with the known observations in the case of two other well-known *cis-trans* systems, *viz.*, oleic-elaidic and erucic-brassidic.

Experimental

I. The oil, in each case, was obtained by extraction of the seeds with benzene, steam distillation to remove the volatile portion and final purification with dilute carbonate solution. The fatty acids, obtained as usual,

were separated into solid and liquid portions by lead salt separation, most of the non-saponifiable matter in the case of cumin and dill being removed before working up the soap for acids. The constants of the oil, the solid and liquid acids are:—

		Cumin	Dill	Ajowan
Pure oil	Sap. value	183·4	173·4	189·3
	Iod. value	94·34	93·54	101·3
	N. S. matter	9·5	8·6	2·9
Solid acids	p.c. of total acids	30·2	50·9	43·1
	Acid value	197·7	201·9	198·9
	Iod. value	59·92	76·63	84·16
Liquid acids ..	p.c. of total acids	69·8	49·1	56·9
	Acid value	193·5	190·5	186·8
	Iod. value	118·4	110·9	124·6

Note.—1. I. V. determinations by Hanus method.
2. The liquid acids still contained small quantities of non-saponifiable matter.

II. The fatty acid composition was determined by ester fractionation.

Cumin .. Palmitic 3·4%, stearic 3·3%, arachidic 4·9%, petroselinic 21·3%, oleic 39·3% and linoleic 27·9% by weight.

Dill .. Myristic 0·6%, palmitic 6·7%, stearic traces only, petroselinic 44·8%, oleic 34·4% and linoleic 13·3% by weight.

Ajowan .. Palmitic 2·6%, petroselinic 41·8%, oleic 34·8% and linoleic 20·7% by weight.

Petroselinic acid[2] was confirmed in each case by saponifying its ester and oxidising the liberated acid with alkaline permanganate. The different samples of the dihydroxy acid (m.p. 122°) obtained from the three different fats, were mixed with one other and the m.p. in each case showed no depression. Oleic and linoleic acids were confirmed by means of their hydroxy derivatives.

III. *Tetracetate oxidation of* 6:7-*dihydroxy stearic acid.*—1·6 gm. of the hydroxy acid were suspended in dry benzene (30 c.c.), 2 gm. of lead tetracetate added and the mixture shaken on a mechanical shaker. After about 15 minutes almost the whole of the solid disappeared and afterwards a white solid began to separate. At the end of 45 minutes the benzene solution was filtered from the insoluble matter, the residue washed with benzene and the washings added to the original filtrate. The residue after removing benzene which was previously washed with water, was treated with excess of semicarbazide hydrochloride-sodium acetate in dilute alcohol, heated

on the water-bath for 2 hours, cooled and diluted. The precipitate was collected, shaken with light petrol and filtered. The product, crystallised from dilute alcohol, had a melting point of 102°, the melting point of lauric aldehyde being[2] 100–1°. The petroleum-ether solution yielded a small quantity of lauric acid, m.p. 43°.

The aqueous washings of the benzene solution were concentrated to a small bulk and treated with a concentrated solution of semicarbazide hydrochloride-sodium acetate. After heating on the water-bath for a short time, the solution was cooled and the solid collected. It crystallised from water in colourless plates, m.p. 178–79° and was soluble in bicarbonate solution. Analysis proved it to be adipic semialdehyde semicarbazone (Found C, 45·04% and H, 7·18%. $C_7H_{13}N_3O_3$ requires 44·92 and 6·95% respectively).

The solid that separates during the oxidation is the lead salt of adipic acid. The salt was decomposed with dilute hydrochloric acid, lead chloride removed and the filtrate evaporated to dryness on the water-bath. The residue, on crystallisation from benzene, melted at 150° and showed no depression with pure adipic acid (149–50°).

IV. *Per-acid oxidation.*—Pure petroselinic acid was obtained from ajowan seed fatty acids and was crystallised at 0° from dilute alcohol. The acid, thus purified, showed a m.p. 28–29° and an I.V. 88·5 (theory 90). Petroselaidic acid was prepared as follows: To one gm. of Poutet's reagent, cooled by ice water, was added 12 gm. of pure petroselinic acid and the mixture stirred well. After maintaining the mixture at 10° for half-an-hour, it was left overnight at the room temperature. The resulting solid mass was ground well with water, filtered, washed free of mineral acid and dried at the pump. It was dissolved in a small volume of hot dilute alcohol and allowed to cool slowly. The separated solid was collected, spread on a filter-paper and pressed well to remove adhering petroselinic acid. The crystallisation was repeated until an almost pure product of m.p. 50–52° was obtained. On oxidation with alkaline permanganate at 20–23° a dihydroxy acid melting at 115–17° was obtained.

To a mixture of 0·5 c.c. of concentrated sulphuric acid and 0·4 c.c. of water, cooled by ice-salt mixture, was added 1·5 gm. of 80% barium peroxide in 3 portions. The cold paste was added to a suspension of 1·8 gm. of petroselinic acid in 25 c.c. of 90% formic acid cooled by ice water. The mixture was shaken well and allowed to warm up gradually. In a few minutes the temperature rose to 35° and was maintained for 2 hours at 38–40°, by surrounding with warm water. After leaving the mixture overnight at room temperature, it was poured into water and extracted with

ether. The hydroxy-formoxy compound thus obtained was refluxed for 3 hours with 25 c.c. of 2N-alcoholic potash, alcohol removed and acidified with hydrochloric acid. The resulting acid, after crystallisation from alcohol, gave m.p. 115–17° and molecular weight 313 as against the theoretical value 314. The melting point was not depressed on mixing with the hydroxy acid obtained by alkaline permanganate oxidation of petroselaidic acid.

The peracetic oxidation was carried out exactly as above, using acetic acid instead of formic acid. The dihydroxy acid obtained melted at 115–17°.

Petroselaidic acid, on oxidation either with peracetic or performic acid, gave a dihydroxy acid of m.p. 122° undepressed by mixing with the dihydroxy acid obtained by alkaline permanganate oxidation of petroselinic acid.

Summary

The naturally occurring *cis*-petroselinic acid gave the lower melting dihydroxy acid, while the *trans*-isomer gave the higher melting dihydroxy acid on per-acid oxidation.

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HETEROCYCLIC COMPOUNDS

Part I. Experiments in Isatins

By K. N. Menon, F.A.Sc. and P. S. Raman

(*Maharaja's College, Ernakulam and Madras University Laboratory, Guindy*)

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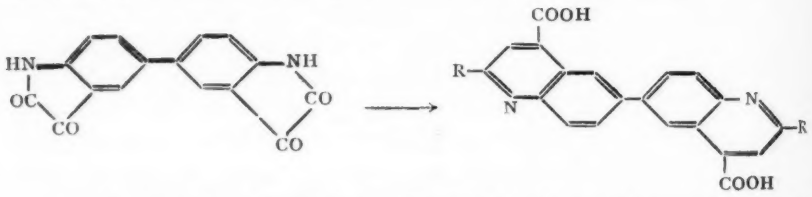
The very important Sandmeyer reaction[1] for the preparation of isatin from aniline has recently been extended by Dethloff and Mix[2] for the preparation of di-isatin from benzidine. The *bis* iso-nitroso compound formed from benzidine, chloral hydrate and hydroxylamine hydrochloride with hydrochloric acid, on treatment with concentrated sulphuric acid at 90–95°, gives di-isatin (5, 5′).

Some of the important reactions of isatin is due to its lactam structure which opens out under the influence of alkali to yield a very reactive α-keto-*o*-amino-carboxylic acid. If the latter is allowed to react with reactive aldehydes and ketones under the influence of alkali, condensation takes place yielding quinoline-4-carboxylic acids.[3] Some of these condensation products, *e.g.*, Atophan from acetophenone and isatin are of importance in chemotherapy.

In view of the great importance of this important reaction, it was considered desirable to investigate it in the field of di-isatins. This report deals with the condensation of di-isatin with some reactive ketones: condensation with acetone, acetophenone, cyclohexanone and α-tetralone all gave diquinoline carboxylic acids according to the following general reaction.



All the condensation products were high melting substances, insoluble in common organic solvents and so could not be purified as such. As an alternative, purification after esterification was tried. The *bis*- (2-methyl cinchoninic acid) and the *bis*-(2-phenyl cinchoninic acid), obtained from di-isatin and acetone and acetophenone respectively, were esterified by

alcohol-sulphuric acid and the esters obtained in a pure form. The *bis*-(tetrahydro acridine-9-carboxylic acid) and the *bis*-(benz-dihydro acridine-9-carboxylic acid), obtained from di-isatin and cyclohexanone and α-tetralone respectively, could not be esterified. This difficulty in esterifying these acids can probably be due to steric hindrance. Jensen and Rethurisch[4] have reported that acridine-9-carboxylic acid cannot be esterified by alcohol-acid method. Borshe[5] has recorded a similar difficulty in esterifying tetrahydro-acridine-9-carboxylic acid. The condensation product of di-isatin with acetoacetic ester could not be obtained pure.

Experimental

The di-isatin was purified by dissolving it in 5% aqueous alkali, just neutralising with glacial acetic acid, filtering off the dark material that separated, and acidifying the solution with hydrochloric acid.

I. *Condensation with acetone.*—2 gm. of di-isatin were dissolved in 22 c.c. of 10% potassium hydroxide and 10 c.c. of acetone added. After distilling off the excess of acetone, the solution was acidified with acetic acid. The precipitated brownish-red solid (2·3 gm.) was soluble in bicarbonate solution and in dilute hydrochloric acid, but insoluble in common organic solvents.

For esterification, 2 gm. of the dry, powdered condensation product was added to a mixture of 50 c.c. of absolute methyl alcohol and 4 c.c. of concentrated sulphuric acid. The resulting solution, after standing overnight at room temperature, was refluxed on the water-bath for 4 hours, cooled and poured on to dilute ammonia and ice. The yellowish solid was stirred into cold, dilute bicarbonate, collected and washed with water. The crude product was refluxed with benzene, the solution filtered free of a dark insoluble matter, and the solvent removed. The residue crystallised in yellowish plates from methyl alcohol and melted at 229–31°. The ester shows a greenish blue fluorescence in benzene and methyl alcohol (Found: C, 71·81; H, 5·18. $C_{24}H_{20}O_4N_2$ requires C, 72·00, H, 5·00).

II. *Condensation with acetophenone.*—3 gm. of di-isatin were dissolved in 35 c.c. of 10% aqueous alcoholic potash, 3 c.c. of acetophenone added, the mixture refluxed for 5 hours, diluted and acidified with acetic acid. The resulting yellow solid (4·2 gm.) was soluble in bicarbonate but insoluble in dilute hydrochloric acid and in common organic solvents.

One gm. of the dry powdered substance was treated with 50 c.c. of absolute alcohol containing 25 c.c. of concentrated sulphuric acid. The substance dissolved with a green fluorescence. The solution was kept at

room temperature for 40 hours, then refluxed on the water-bath for 7 hours, cooled, poured on to ice and basified with ammonia. The yellow solid was immediately filtered and washed with water. The ester was dissolved in benzene and clarified with charcoal, and the solvent removed. The residue crystallised from acetic acid in glistening yellow plates melting at 249–51°. (Found: C, 77·96; H, 5·39. $C_{36}H_{28}N_2O_4$ requires C, 78·27, H, 5·07).

III. *Other condensations.*—Condensation of di-isatin with cyclohexanone and α-tetralone was carried out as given for acetophenone. The products were soluble in bicarbonate solution but all attempts at purification gave no encouraging results. Esterification also failed.

SUMMARY

The Pfitzinger condensation of di-isatin with some ketones is reported.

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DEHYDRATION OF CASTOR OIL BY SUBSTITUTED SULPHONIC ACIDS AND THEIR SALTS

By Dr. K. K. Dole and V. R. Keskar
(*Department of Chemistry, Fergusson College, Poona*)

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A large number of substances are being used as catalysts for the dehydration of castor oil, and the literature is full of the various substances that have been used as catalysts, many of which have been patented. The catalysts used so far can be conveniently classified into the following groups:

(1) Sulphuric acid and its salts.
(2) Phosphoric acid and its salts.
(3) Metallic oxides and salts.
(4) Metallic soaps and other fatty acids.
(5) Dimethyl and diethyl sulphates.
(6) Acid clays.

Sulphuric acid is used as a catalyst in many instances and even a continuous process for the dehydration of castor oil using sulphuric acid as a catalyst has been described in some patents. Sodium bisulphate is more generally used as a catalyst as free sulphuric acid gives very dark coloured products. The catalysts from other groups are also used with varying success. In the present investigation some sulphonic acids and their salts, which have not been previously investigated are employed as catalysts for the dehydration of castor oil. Some of them have been found to be very effective as dehydrating catalysts and some of them give very pale coloured products.

Experimental

The dehydration of castor oil is carried out under two different sets of conditions.

(1) Under atmospheric pressure, and (2) Under reduced pressure.

Dehydration under atmospheric pressure

50 gm. of castor oil were taken in a round-bottomed wide-mouth flask of 250 c.c. capacity. The exact quantity of catalyst (mentioned in the individual experiments) was weighed and added to the flask. The catalyst was mixed with the oil by stirring. A thermometer was suspended in the oil. Carbon dioxide was bubbled through the oil in order to have an inert

atmosphere. The flask was directly heated on a wire-gauze. The temperature of the reaction was attained in 5–10 minutes; it was maintained by adjusting the flame, within the limit of $\pm$ 5° C. The samples were drawn at different intervals of time and the necessary characteristic values of the samples were determined.

Dehydration under reduced pressure

100 gm. of the oil mixed with the appropriate quantity of the catalyst, were taken in a 500 c.c. round-bottomed pyrex flask. It was fitted with a rubber cork with two holes; one for the thermometer that was suspended in the oil as before and the other for a delivery tube. The delivery tube was connected through a water condenser, two traps, an anhydrous calcium chloride tower and a manometer to a vacuum pump. In between the two traps a wash bottle containing a concentrated sodium hydroxide solution was placed to absorb the acidic decomposition products. The oil was heated by a direct flame. The temperature was attained in 10–15 minutes, as the heating was required to be done slowly due to heavy frothing of the oil. Porous pieces were added in order to keep the mass constantly boiling. The heating was stopped after the requisite time and the oil was cooled under reduced pressure.

The extent of dehydration was followed by determining the Iodine value and the hydroxyl value of the dehydrated oil. In addition the following values of the oil were also determined: acid value, diene value, molecular weight, refractive index, colour, viscosity, saponification value and drying time. Acetyl value and unsaponifiable matter in the oil was also determined in some experiments.

As the dehydrated castor oil contains some amount of conjugated fatty acids, the iodine value by Wij's method does not give the total amount of unsaturation present in the oil. The results obtained by the Woburn method[1] are more reliable and therefore, it has been used in the present work. The hydroxyl value[2] was determined by using the pyridine-acetic anhydride mixture. The percentage of conjugated fatty acids was found out by the Elis and Jones method[3] using maleic anhydride-in-toluene as the reagent. The molecular weights were determined cryoscopically by observing the depression in freezing point of benzene. Refractive index was found out at 40° C. on Abbe's refractometer. The viscosity of the oil was determined by a modified type of Ostwald viscometer, having a capillary of 1·352 mm. in diameter. Other values were found out by standard methods. The percentage of conjugated fatty acids in the dehydrated oils was determined (in some samples) by using the ultraviolet absorption spectra.

Results

The characteristic values of the dehydrated samples obtained by using different sulphonic acids are given in the following table (Table I). The percentage of the catalyst was 0·3% except the one marked with (*) which was 1%. The temperature of heating was 250° C. while with the catalyst marked with * the temperature was 290° C. The time of heating in all cases was 60 minutes.

The rate of dehydration as studied from the increase in the Iodine value (Woburn) is given in Table II.

Table I

No.	Catalyst (acid)	*I.V.*	*H.V.*	*A.V.*	*Mol. wt.*	Ref. Index 40 C.	Colour			% Conjugation
							B	*R*	*Y*	
1	Benzene sulphonic ..	147	51	37	938	1·4655	9	15	12	22
2	*p*-toluene sulphonic..	138	60	16·6	..	1·4641	2·7	14	16	16·8
3	*p*-xylene sulphonic ..	123	93	6	943	1·4629	1	14	16	..
4	Sulpho salicylic ..	138	40	15·7	913	1·4662	3	15	14	18·5
5	*m*-sulpho benzoic ..	151	40	47	845	1·4711	9	16	22	28·6
6	Phenol sulphonic ..	134	54	6	980	1·4710	8	10	15	18
7	Sulpha anilic* ..	130	43	17	..	..	3	14	15	..

I.V.—Iodine value; *H.V.*—Hydroxyl value; *A.V.*—Acid value; *Mol. wt.*—Molecular weights; Colour: *B*-Blue; *R*-Red; *Y*-Yellow.

The numbers of the catalysts in Table II are given according to their number in Table I.

Table II

No.	Catalyst No. as in Table I	Iodine values of the samples drawn at the time intervals in minutes as below :						
		10	20	30	40	50	60	70
1	1	107	119	128	135	142	146	146
2	2	107	108	118	129	132	136	138
3	3	98	105	111	116	120	123	..
4	4	109	117	123	130	132	134	138
5	5	115	130	143	152	152	151	..

The behaviour of the catalysts under reduced pressure is summarised in Table III.

TABLE III

No.	Catalyst No.	Press. mm.	Temp. C.	Time min.	*I.V.*	*H.V.*	*A.V.*	*Mol. wt.*	*Ref. Ind.* 40 C.
1	1	35	225	90	130	61	8·3	947	1·4632
2	2	25	250	70	140	38	6·8	..	1·4720
3	3	20	250	60	124	81	3·8	917	1·4705
4	4	20	270	60	143	28	8·2	930	1·4666
5	5	30	250	100	137	58	12	920	1·4652
6	6	20	250	60	148	55	7·4	930	1·4730

The effect of substitution of various groups in the benzene ring on the catalytic activity of a substance is studied and the results are given in Table IV.

TABLE IV

No.	Catalyst No. as in Table I	Group substituted	Conditions			*I.V.*	*A.V.*	*H.V.*
			Time min.	Temp. °C.	% cata.			
1	1	..	60	250	0·3	147	37	51
2	2	$-CH_3$	70	250	0·3	138	16	60
3	3	$(CH_3)_2$	60	250	0·3	123	6	93
4	4	$-OH$, $-COOH$	60	250	0·3	138	15	40
5	5	$-COOH$	50	250	0·3	152	40	35
6	6	$-OH$	60	250	0·3	134	6	54
7	7	$-NH_2$	60	290	1·0	130	17	43
8	Sulphuric acid	..	60	225	0·3	139	8	38

PART II

Salts of sulphonic acids

The free acids used so far are active catalysts. However, they have a tendency to decompose the oil as a result of which they give dark coloured products. In order to overcome this defect it was proposed to use the

sodium or potassium salts of the sulphonic acids instead of the free acids. A number of salts have been tried but a very few of them are found useful.

All the salts remained solid at the temperature of reaction. They showed no activity or in some cases negligible activity. Some salts of phenol sulphonic acid showed definite activity, whereas potassium phenol sulphonate was quite active and gave complete dehydration. The influence of salts of sulphonic acids as dehydrating catalysts is given in the following two tables.

TABLE V

No.	Catalyst	Condition of heating			Iodine Values (Woburn)
		%	Temp. C.	Time (mins.)	
1	Sodium benzene sulphonate ..	1	250	30	90
2	Sodium *p*-toluene sulphonate ..	1	250	60	93
3	Sodium *p*-xylene sulphonate ..	1	250	60	91
4	Sodium sulphosalicylate ..	0·6	300	40	91
5	Sulphosalicylic acid $\frac{2}{3}$ neutralized ..	0·6	285	40	119
6	,, acid $\frac{1}{3}$,, ..	0·6	265	40	129
7	Sodium sulpho-benzoate ..	1	310	30	91
8	Potassium hydrogen sulpho-benzoate ..	0·4	310	40	136
9	Sodium *m*-nitrobenzene sulphonate ..	1	250	40	86
10	Sodium naphthalene 1-sulphonate ..	1	250	90	85
11	Sodium 1-naphthol 5-sulphonate ..	1	250	30	86
12	Sodium 2-naphthol 1-sulphonate ..	1	250	30	90
13	Sodium 2-naphthol 6-sulphonate ..	1	250	30	89
14	Sodium 6-naphthyl amine 6-sulphonate ..	1	250	30	93
15	Sodium 1-naphthyl amine 2-sulphonate .	1	250	40	105
16	Sodium anthraquinone 2:6 disulphonate ..	1	250	60	90
17	Sodium anthraquinone 2:7 disulphonate ..	1	300	30	92
18	Sodium anthraquinone 2-sulphonate ..	1	300	30	90

Salts of phenol sulphonic acid

(1) Sodium salt.

(2) Barium salt.

(3) Magnesium salt.

(4) Potassium salt.

The abovementioned salts of *o*-phenol sulphonic acid were investigated as catalysts. The sodium and barium salts were slightly active, the potassium salt was very active while, the magnesium salt was inactive.

The comparative account of the activity of the catalysts as studied from the increase in the unsaturation of the oil is given in the following table the detailed account of the potassium salt as a catalyst is published elsewhere.*

* 6th *Proceedings of the Oil Technologists' Association*, India, Kanpur, 1950.

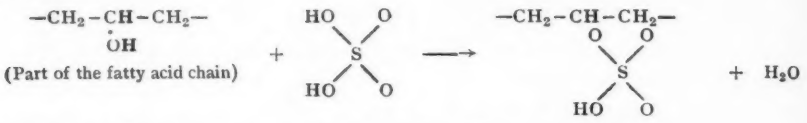
TABLE VI

Dehydration by salts of o-phenol sulphonic acid

No.	Catalyst	Conditions of dehydration			Iodine Value Woburn
		%	Temp. C.	Time (min.)	
1	Sodium salt ..	1	250	30	92
2	do ..	1	310	30	120
3	Barium ,, ..	1	250	30	117
4	Magnesium ,, ..	1	300	30	91
5	Pottassium ,, ..	1	270	60	134
6	do ..	3	215	60	153

DISCUSSION

The dehydration of castor oil as studied in this investigation is a catalytic process. The action of the catalyst is that of a formation of an intermediate ester with the —OH group of the ricinoleic acid, removing the molecule of water. The intermediate ester subsequently breaks up at high temperature inserting one double bond at the carbon atom containing the hydroxyl group. The mechanism of the reaction has been studied by Forbes and Neville.[4] The reaction in the case of sulphuric acid is represented as follows:



The ester breaks to:— —CH = CH—CH_2— and H_2SO_4

This mode of representation can be applied to all the acid catalysts in general the general formula of the catalyst being X—OH. Acids such as sulphuric and sulphonic can be represented as X—SO_2OH, sulphuric acid then can be regarded as hydroxy sulphonic acid $HO \cdot SO_2 \cdot OH$. The sulphonic acids may be acting in the same manner as sulphuric acid, since they are very similar to sulphuric acid in their activity; they are effective in small concentrations, give dark coloured products and have a tendency of decomposing the castor oil. Since sulphuric acid is a hydroxy sulphonic acid $HO \cdot SO_2OH$, the hydroxyl groups are capable of forming the intermediate ester.

In sulphonic acids one of the OH groups is substituted by alkyl or aryl radical but the OH from SO_2OH is still free to form an intermediate ester. The alkali bisulphates which are active dehydrating catalysts can be represented as $NaO \cdot SO_2OH$, etc. It is obvious, therefore, that the OH group in the salt is capable of forming the intermediate ester. The salts of sulphonic acids are not effective as catalysts except potassium phenol sulphonate. Similarly, normal salts of sulphuric acid are inactive. The absence of activity in the salts of sulphonic acids may be due to the fact that they do not contain any hydroxyl group capable of producing the intermediate unstable ester. Potassium phenol sulphonate melts at the temperature of reaction and probably the potassium atom may be migrating to the phenolic OH group keeping the SO_2OH free to form the intermediate ester.

Effect of substitution of various groups in the benzene ring of aromatic sulphonic acids.

As stated above all the aromatic sulphonic acids can be represented by the general formula $X \cdot SO_2OH$, wherein X is the substituted benzene ring. Various sulphonic acids containing groups such as —COOH, —OH, —CH_3. —NH_2 substituted in the benzene ring are investigated here. The results are given in Table IV. Benzene sulphonic acid is a reactive catalyst; with 0·3% catalyst the reaction is complete in 60 minutes. Another equally vigorous catalyst is *m*-sulpho benzoic acid. The introduction of —COOH group increases the activity and the reaction is complete in 50 minutes. However, the acid value in the case of both the catalysts is very high. The introduction of CH_3 group in the ring gives progressively less and less decomposition. The acid value in the case of benzene-, toluene- and xylene-sulphonic acids are 36, 16, and 6 respectively. The colour of the products becomes progressively pale. But the activity of the catalyst is greatly reduced. Consequently, xylene sulphonic acid does not give complete dehydration. The introduction of —OH group in the ring mitigates the tendency of decomposition without affecting the dehydrating capacity of the catalyst. Thus phenol sulphonic acid gives comparatively paler products than benzene sulphonic acid. This is also verified in the case of sulphosalicylic acid wherein both —OH and —COOH groups are introduced. The introduction of —NH_2 group greatly impairs the activity of the catalyst. This may probably be due to the internal linking of the amino group in the molecule with the sulpho-group (SO_2OH).

Summary of Conclusions

(1) Sulphonic acids and some of their salts containing acidic OH groups are useful as catalysts for the dehydration of castor oil.

(2) Sulphonic acids are effective in small concentrations from 0·1 to 0·3% of the oil. The percentage of the catalyst required varies with the choice of the catalyst.

(3) The introduction of —COOH group in the benzene ring increases the activity of the catalyst but the rate of decomposition of the oil also increases when the —COOH group is introduced.

(4) The introduction of —OH group in the benzene ring mitigates the decomposing tendency of the catalyst without much affecting the dehydrating tendency of the catalyst.

(5) The introduction of $—CH_3$ group decreases the activity of the catalyst. With the introduction of more and more $—CH_3$ groups the gradual decrease in the activity is observed. Thus benzene sulphonic acid is the most active, whereas, *p*-xylene sulphonic acid is the least active catalyst.

(6) The introduction of NH_2 group in the benzene ring greatly reduces the dehydrating capacity of the substance.

(7) Potassium salt of phenol sulphonic acid is a good dehydrating agent.

(8) A number of sodium salts of sulphonic acids are investigated. They are found to be inactive, probably due to the absence of any acidic OH group in the molecule.

(9) Castor oil dehydrated under reduced pressure is always pale in colour and low in acid number than the oil dehydrated under atmospheric pressure.

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THE MOTION OF FOUR RECTILINEAR VORTEX FILAMENTS

By S. K. Lakshmana Rao

(*Department of Power Engineering, Indian Institute of Science, Bangalore-3*)

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1. Introduction

The motion of three parallel rectilinear vortex filaments of strengths K_1, K_2, K_3 in a perfect incompressible fluid extending to infinity originally examined by Gröbli (1877) has been again considered by Synge (1949) who has made an exhaustive study of the motion by representing the various configurations of vortices by points in trilinear co-ordinates on a representative plane. A similar study of all the motions of four vortex filaments presents great difficulty owing to the very large number of cases to be dealt with and the lack of corresponding geometrical representation adequate for classifying all the motions. The problem of four vortex filaments which form fixed configurations, *i.e.*, configurations with fixed sides and diagonals was previously examined (1951). Synge's method can however be used for the study of motions of four vortex filaments by making some simplifying assumptions. We study in particular the case where the configuration is initially a parallelogram and the vortices at the ends of diagonals are of equal strength.

By taking the adjacent sides and a diagonal which completely specify the configuration as the geometrical magnitudes, it is possible to classify all the motions in a manner similar to Synge's and the present paper deals with this problem. The theory resembles that of the motion of three vortices in many respects, but it is felt that it may be of interest to see the changes due to the presence of an additional vortex. Under the more particular case of rectangular configuration with special choice of vortex strengths, the motion is examined by representing the configurations by Cartesian co-ordinates.

2. Equations of Motion

Vortices of strengths K_1, K_2, K_1, K_2 lie initially at the corners A, B, C, D of a parallelogram. Let a, c and b, g be the adjacent sides and diagonals respectively, the diagonal b joining the vortices K_1, K_1 and g joining

K_2, K_2. Then these vortices remain at the corners of a parallelogram at the end of any time (Gorjatschaff, 1898). The configuration is uniquely determined by the magnitudes a, b, c except for orientation and the motion of the vortices is represented by a point on a representative plane by trilinear co-ordinates.

The following equations of motion of the vortices have been obtained by Lakshmana Rao (1951).

$$\frac{da}{dt} = S\,a^{-1}\,[K_1\,(b^{-2} - c^{-2}) - K_2\,(g^{-2} - c^{-2})] \tag{2.1}$$

$$\frac{db}{dt} = S\,b^{-1}\,[2K_2\,(c^{-2} - a^{-2})] \tag{2.2}$$

$$\frac{dc}{dt} = S\,c^{-1}\,[K_1\,(a^{-2} - b^{-2}) - K_2\,(a^{-2} - g^{-2})] \tag{2.3}$$

where S = area of the parallelogram ABCD.

We have the integrals due to Kirchhoff (Lamb, 1945).

$$2K_1K_2 \log ac + K_1^2 \log b + K_2^2 \log g = \text{const.} = \alpha \tag{2.4}$$

$$K_1b^2 + K_2g^2 = \text{const.} = \beta. \tag{2.5}$$

3. VARIABLE CONFIGURATIONS

Following Synge's procedure we write

$$x_1 = a \,/\, (a + b + c) \tag{3.1}$$

$$x_2 = b \,/\, (a + b + c) \tag{3.2}$$

$$x_3 = c \,/\, (a + b + c) \tag{3.3}$$

and take x_1, x_2, x_3 to signify the trilinear co-ordinates of a point with an equilateral triangle of unit attitude for the triangle of reference so that

$$x_1 + x_2 + x_3 = 1. \tag{3.4}$$

For any parallelogram configuration we have definite values of a, b, c giving a unique representative point x_1, x_2, x_3. For a given x-point we have an infinity of similar parallelogram configurations. As in Synge's theory of three vortices, the possible collinear configurations correspond to points on the lines of join of the middle points of the reference triangle. Essentially there are two distinct collinear configurations only. Differentiation of the equations (3.1), (3.2), (3.3) gives

$$\frac{dx_1}{dt} = \frac{da}{dt}\,(a + b + c)^{-1} - a\,(a + b + c)^{-2}\left(\frac{da}{dt} + \frac{db}{dt} + \frac{dc}{dt}\right)$$

and two similar equations. It is seen that

$$\frac{dx_1}{dt} = \mathrm{K}\mathrm{G}_1, \quad \frac{dx_2}{dt} = \mathrm{K}\mathrm{G}_2, \quad \frac{dx_3}{dt} = \mathrm{K}\mathrm{G}_3$$

with

$$\mathrm{K} = \mathrm{S}\,(a+b+c)^4\,(abcg)^{-2}, \tag{3.5}$$

$$\mathrm{G}_1 = -\,\mathrm{K}_1 x_1\,(x_2^2 - x_3^2)\,x^2 + \mathrm{K}_2 x_1\,(x^2 - x_3^2)\,x_2^2 + x_1\theta \tag{3.6}$$

$$\mathrm{G}_2 = -\,2\mathrm{K}_2 x_2\,(x_3^2 - x_1^2)\,x^2 + x_2\theta \tag{3.7}$$

$$\mathrm{G}_3 = -\,\mathrm{K}_1 x_3\,(x_1^2 - x_2^2)\,x^2 + \mathrm{K}_2 x_3\,(x_1^2 - x^2)\,x_2^2 + x_3\theta \tag{3.8}$$

and

$$\theta = \mathrm{K}_1 x_1\,(x_2^2 - x_3^2)\,x^2 + 2\mathrm{K}_2 x_2\,(x_3^2 - x_1^2)\,x^2 + \mathrm{K}_1 x_3\,(x_1^2 - x_2^2)\,x^2 - \mathrm{K}_2 x_1\,(x^2 - x_3^2)\,x_2^2 - \mathrm{K}_2 x_3\,(x_1^2 - x^2)\,x_2^2, \tag{3.9}$$

where

$$g\,/\,(a+b+c) = x, \tag{3.10}$$

so that

$$x^2 = 2x_1^2 - x_2^2 + 2x_3^2. \tag{3.11}$$

The differential equations

$$\frac{dx_1}{\mathrm{G}_1} = \frac{dx_2}{\mathrm{G}_2} = \frac{dx_3}{\mathrm{G}_3} = \mathrm{K}dt. \tag{3.12}$$

give the motion of the representative point. They define a congruence of x-curves giving the behaviour of the configurations and also the rate of change while the size of the configuration is given by one of the integrals (2.4), (2.5).

The following results are then simply deduced.

If the strengths of the vortices do not satisfy the relation

$$\mathrm{K}_1^2 + \mathrm{K}_2^2 + 4\mathrm{K}_1\mathrm{K}_2 = 0 \tag{3.13}$$

and α is known from the initial configuration (equation 2.4) to each x-point there corresponds a unique parallelogram configuration except for orientation. Whereas if they satisfy the relation (3.13) then to each point on the conic (hyperbola)

$$\mathrm{K}_1 x_2^2 + \mathrm{K}_2 x^2 = 0 \tag{3.14}$$

there corresponds a single infinity of parallelogram configurations of both orientations, and to a point off this conic there corresponds a unique parallelogram configuration except for orientation.

4. SINGULAR POINTS

The equations

$$G_1 = -K_1x_1(x_2^2 - x_3^2)x^2 + K_2x_1(x^2 - x_3^2)x_2^2 + x_1\theta = 0 \quad (4.1)$$

$$G_2 = -2K_2x_2(x_3^2 - x_1^2)x^2 + x_2\theta = 0 \quad (4.2)$$

$$G_3 = -K_1x_3(x_1^2 - x_2^2)x^2 + K_2x_3(x_1^2 - x^2)x_2^2 + x_3\theta = 0 \quad (4.3)$$

give the singular points of the representation curves. Under the condition $K_1 + K_2 = 0$ the collisions of unequal vortices, *viz.*, the cases $x_1 = 0$, $x_2 = x_3 = \frac{1}{2}$ and $x_3 = 0$, $x_1 = x_2 = \frac{1}{2}$, $x_3 = 0$ are seen to correspond to singular points.

To see any other singular points we first consider the case where $\theta = 0$. Then from (4.2) we see that $x_1 = x_3$ and additionally (4.1) or (4.3) gives

$$K_1(x_2^2 - x_1^2)x^2 - K_2(x^2 - x_1^2)x_2^2 = 0 \quad (4.4)$$

The case $x_1 = x_2 = x_3$ is seen to be exceptional and is to be ruled out.

In the case of $\theta \neq 0$, we have $x_1 \neq x_3$. We have then the easily obtainable relation

$$\theta(K_1^2 + 4K_1K_2 + K_2^2) = 2K_2(x_3^2 - x_1^2)(K_1x_2^2 + K_2x^2) \quad (4.5)$$

In case equation (3.13) holds we are led to equation (3.14)

$$K_1x_2^2 + K_2x^2 = 0.$$

We have thus the results:

If

$$K_1^2 + K_2^2 + 4K_1K_2 \neq 0 \quad (4.6)$$

and

$$K_1 + K_2 \neq 0 \quad (4.7)$$

the singular points arise when $x_1 = x_3$ corresponding to rhombus configurations. The case $x_1 = x_2 = x_3$ corresponding to an angle of 60° in the rhombus is an exceptional case.

If

$$K_1^2 + K_2^2 + 4K_1K_2 = 0 \quad (4.8)$$

we necessarily have (4.7) and the singular points lie on the hyperbola

$$K_1x_2^2 + K_2x^2 = 0.$$

If

$$K_1 + K_2 = 0 \quad (4.9)$$

(4.6) is necessarily true and the only singular points are when $x_1 = 0$, $x_2 = x_3 = \frac{1}{2}$ or $x_3 = 0$, $x_1 = x_2 = \frac{1}{2}$ corresponding to collisions in pairs of unequal vortices.

5. Rectangular Configuration

If vortices of strengths K, − K, K, − K lie at the corners of a rectangle initially, they do so at the end of any time (Lamb, 1945) and the configuration can never pass through collinearity. The initial orientation is thus reserved for all time.

To study the motion we may write

$$a = x,\ c = y \qquad 0 < x,\ y < \infty$$

and take (x, y) as the rectangular cartesian co-ordinates of a point on a representative plane. The co-ordinate axes are non-reachable barriers for the motion of (x, y).

The equations of motion are easily seen from (2.1), (2.3) to be

$$-\frac{dx}{x^3} = \frac{dy}{y^3} = \frac{2K}{xy\,(x^2 + y^2)}\,dt.$$

The representative point moves on the curve

$$x^{-2} + y^{-2} = \text{const.} = 1/d^2$$

which is equivalent to the integral (2.4).

This congruence of curves has no singularities and the configuration cannot remain fixed.

In conclusion, I am indebted to Prof. B. S. Madhava Rao for originally suggesting the problem, for helpful criticism and encouragement. My thanks are due to the Professor of Civil and Hydraulic Engineering for his kind interest in this work.

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STUDIES IN COLLOID OPTICS*

Part III. Sol-Gel Transition of Some Lyophobic Gels

BY P. K. KATTI

(Lecturer in Physics, Delhi Polytechnic)

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1. INTRODUCTION

IN two earlier papers[1, 2] the author has discussed some preliminary results on the sol-gel transition of agar-agar and gelatin gels, obtained by using the R. S. Krishnan[3] technique. These results showed that it would be worthwhile to make an extensive study under different conditions of temperature, concentration, electrolyte content, etc., of different types of gels by this technique, in order to get a clearer picture of the mechanism of the phenomenon of sol-gel transition. The present paper gives a very brief account of the investigations on three lyophobic gels, *viz.*, Aluminium Molybdate, Zirconium and Ferric Succinate gels, further details of which are discussed in the author's Doctorate Thesis (1951).[4]

2. R. S. KRISHNAN EXPERIMENTAL TECHNIQUE

A complete description of our experimental arrangement is given in an earlier paper.[1] It may be recalled that ρ_u, is the depolarisation of light scattered at right angles to the incident beam when the latter is unpolarised ρ_v is the depolarisation of light scattered at right angles to the incident beam when the latter is polarised with its electric vector vertical ($\rho_v = 0$ for spherically symmetric particles and increases with the increase in the asymmetry of the particles), ρ_h is the depolarisation of the light scattered at right angles to the incident beam when the latter is polarised with its electric vector horizontal ($\rho_h = 100\%$ for very small particles and decreases with the increase in the size of the particles). I_z is the intensity of light scattered at right angles to the incident beam which is polarised with its electric vector vertical. I_δ is the density scattering computed from the relation

$$I_\delta = I_z \cdot \frac{3 - 4\rho_v}{3 + 3\rho_v}$$

* These investigations were made while the author was working for his doctorate under Dr. L. A. Ramdas at the Meteorological Office, Poona.

$I_{4\pi}$ is the total light scattered by one centimetre layer of the medium in all directions, *i.e.*, in a solid angle 4π, when the incident beam is unpolarised. $I_{4\pi}$ is expressed as a fraction of the intensity of incident light.

It is easy to show that, during the process of coagulation considered by Smoluchowski,[5] I_8 increases with time during the initial stages, reaches a maximum, and later on tends to decrease again when the total number of scattering centres decreases rapidly, and that the existence of a point of maxima in the I_8-time curve during the earlier stages of the sol-gel transition can at least qualitatively be used to detect the increase in the size of the particles due to aggregation.

3. Preparation of the Sols

The three lyophobic gels discussed in this paper were prepared by the metathetical reaction between the different salts as given below:

	A		B		C		D
(1)	Aluminium chloride	+	Sodium molybdate	=	Aluminium molybdate	+	Sodium chloride
(2)	Zirconium nitrate	+	Sodium succinate	=	Zirconium succinate	+	Sodium nitrate
(3)	Ferric chloride	+	Sodium succinate	=	Ferric succinate	+	Sodium chloride

Pure B.D.H. chemicals were used. Stock solutions occurring on the left-hand side of the above reactions were prepared in dust-free distilled water and were preserved in well steamed glass-stoppered bottles.

On mixing the solutions A and B, a gelatinous precipitate of the product C (see above equation) is obtained which on shaking re-disperses in the supernatant liquid to give a clear sol if an excess of A is present. An excess of solution A thus acts as a peptising agent. This sol is, however, quite unstable and a gradual increase in the viscosity and turbidity of the sol with time continues until both these properties attain constant maximum values when the gel has set completely. It is noticed that (i) the initial sol values of intensity and depolarisation, (ii) the rates of variation of intensity and depolarisation during the sol-gel transition, and (iii) the final structure of the gels, *i.e.*, the final size and shape of the gel particles, its viscosity, etc., are influenced by the temperature at which the transition takes place, the concentration of the sol, *i.e.*, the amount of the colloidal material in the sol, and the excess of the salt A in the sol. In order to obtain a clear picture of the sol-gel transition it is obvious that the influence of each of these factors should be examined. Therefore, the following sols of six different concentrations prepared in three lots *a*, *b* and *c* were used for our investigations.

(i) *Aluminium molybdate gels.*—6 Sols of concentration 2·2%, 2·4%, 2·6%, 3·0%, 3·5% and 4·0% in each group *a*, *b*, *c* containing 0·08 gm.,

0·09 gm. and 0·1 gm. respectively of aluminium chloride in excess per c.c. of the sol.

(ii) *Zirconium succinate gels.*—3 Groups *a*, *b*, *c* of six sols of concentration 1·0%, 1·1%, 1·2%, 1·3%, 1·4% and 1·5% containing 0·03, 0·033 and 0·036 gm. respectively of zirconium nitrate in excess per c.c. of the sol.

(iii) *Ferric succinate gels.*—3 Groups *a*, *b*, *c* of six sols of concentration 0·3%, 0·4%, 0·5%, 0·6%, 0·7% and 0·8% containing 0·006, 0·007 and 0·008 gm. respectively of ferric chloride per c.c. of the sol.

It may be noted that these lyophobic gels can be obtained only in a very narrow range of concentration and that the above sols cover the whole range of concentration and excess of the first component A over which the respective gels can be obtained.

4. Measurement of Intensity and Depolarisation

The particular sol under investigation was prepared in a glass cell and inserted in the path of the incident beam just when the gelatinous precipitate was re-dispersing. Observations for ρ_v and I_z were made from the instant the minimum value of I_z was recorded. During the sol-gel transition measurements for ρ_v and I_z were made alternately. From the I_z-time and ρ_v-time curves the instantaneous values of I_z and ρ_v were read off. The instantaneous values of I_z and ρ_v thus obtained were used to calculate the density scattering. Ferric succinate gels were coloured and therefore a red Wratten filter was introduced in the path of the scattered light throughout the experiments.

5. Discussion of the Results

The sol state.—Table I shows the variation of intensity and depolarisation with concentration for the various sols. The sol values of intensity and depolarisation are observed to be independent of temperature. The values of ρ_h and ρ_v in Table I show that the size and shape of the sol particles is not appreciably affected by concentration or by the excess of the peptising agent. This is also in agreement with the intensity values of the scattered light which varies directly as concentration.

Sol-gel transition.—The main trend of the variations of intensity and depolarisations with concentration, temperature, etc., is similar in the three different lyophobic gels under discussion. It is only the magnitude of the variations that changes from one gel to the other.

Effect of temperature.—Table II (*a*) shows the final values of intensity and depolarisation of a 4·0% aluminium molybdate gel when the sol-gel transition takes place at different temperatures shown in column 1. The

TABLE I

Intensity and depolarisation in the sol state

Concentration %	(a)			(b)			(c)		
	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$
				Aluminium molybdate					
4·0	80	0·6	1·00	85	0·6	0·90	90	0·6	0·90
3·5	80	0·6	0·95	90	0·6	0·90	90	0·6	0·90
3·0	85	0·6	0·85	90	0·6	0·80	90	0·6	0·90
2·6	85	0·6	0·70	90	0·6	0·70	95	0·5	0·70
2·4	90	0·6	0·60	90	0·6	0·60	95	0·5	0·60
2·2	90	0·6	0·50	90	0·6	0·60	95	0·5	0·50
				Zirconium succinate gels					
1·5	90	0·4	0·75	80	0·4	0·70	95	0·3	0·75
1·4	90	0·3	0·70	85	0·4	0·70	95	0·3	0·70
1·3	90	0·3	0·65	90	0·3	0·60	95	0·3	0·68
1·2	95	0·3	0·60	95	0·3	0·58	95	0·3	0·68
1·1	95	0·3	0·55	95	0·3	0·55	95	0·3	0·55
1·0	95	0·3	0·50	95	0·3	0·50	95	0·3	0·50
				Ferric succinate gels					
0·8	90	1·1	0·40	90	1·1	0·39	90	1·1	0·38
0·7	90	1·1	0·35	90	1·1	0·35	95	1·0	0·35
0·6	95	1·0	0·30	95	1·0	0·30	95	1·0	0·30
0·5	95	1·0	0·27	95	1·0	0·27	95	1·0	0·25
0·4	95	1·0	0·22	95	1·0	0·21	95	1·0	0·20
0·3	95	1·0	0·15	95	1·0	0·15	95	1·0	0·15

second and third columns show that ρ_h decreases and ρ_v increases rapidly as the temperature increases. Tables III (*a*) and IV (*a*) show similar variations of ρ_h and ρ_v, for a zirconium succinate and ferric succinate gel respectively. It can be seen that in the case of ferric succinate gels, increase in temperature causes an appreciable increase in asymmetry of the particles,

TABLE II

Intensity and depolarisation of a 4·0% (a) Aluminium Molybdate Gel

Temp. °C.	(a)			(b)		
	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$
10	65	1·4	3·5	65	1·4	3·5
20	65	1·4	3·5	65	1·4	3·5
30	60	1·6	3·8	65	1·4	3·5
40	55	2·2	5·3	63	1·5	3·6
50	50	2·8	8·9	58	1·9	3·9
60	40	4·8	12·3	50	2·8	8·8

ρ_v increasing from 1·8% to 10% as the temperature increases from 15° C. to 50° C.

Effect of increase in temperature on gels which have completely set at a lower temperature.—Table II (*b*) shows the final values of intensity and depolarisation which a 4·0% aluminium molybdate gel, first completely set at 10° C. and then raised to the temperature mentioned in column 1, will attain if it is allowed to stand for sufficient time at that temperature. The 4·0% sol was allowed to stand at 10° C. for a few hours so as to allow it to set completely at 10° C. It was then raised to the temperature in column 1 and allowed to stand for sufficient time so that ρ_h, ρ_v and intensity attained constant values.

It may be noted that while Table II (*a*) shows the values of ρ_h, ρ_v, and $I_{4\pi}$ for gels prepared at the different temperatures (the complete sol-gel transition from the sol to the gel state taking place at the particular temperature given in the first column), Table II (*b*) shows the intensity and depolarisation for a gel of the same concentration first completely set at 10° C. and then raised to the corresponding temperature. The difference in the values of intensity and depolarisation is therefore due to the fact that in the latter the changes in the size and shape of the particles at any temperature are taking place in a highly viscous medium, *i.e.*, in the gel set at 10° C., while in the former the viscosity of the sol is almost negligible in the earlier stages of increase in the size during the sol-gel transition. Tables III and IV show similar results for zirconium and ferric succinate gels.

TABLE III

Intensity and depolarisation for a 1·5% (*a*) *Zirconium Succinate Gel*

Temp. °C.	(*a*)			(*b*)		
	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$
30	60	2·0	4·8	60	2·0	4·8
40	55	2·3	7·0	58	2·2	6·0
50	43	3·0	9·8	50	2·6	8·3
60	33	4·0	11·4	45	2·8	9·8
70	28	5·3	15·5	38	3·5	10·2

TABLE IV

Intensity and depolarisation for a 0·8% (*a*) *Ferric Succinate Gel*

Temp.°C.	(*a*)			(*b*)		
	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$
15	75	1·8	2·5	75	1·8	2·5
25	70	2·5	2·9	73	2·2	2·7
35	60	5·3	3·5	65	4·4	3·4
45	45	9·5	3·9	55	7·6	3·6
50	40	10·0	4·3	50	7·8	3·7

Effects of concentration and peptising agent.—Table V shows the intensity and depolarisation of gels of different concentration belonging to the three groups *a*, *b* and *c* referred to in para 3. On comparing the values of ρ_h and ρ_v at different concentrations it is noticed that ρ_h decreases and ρ_v increases with increase in the concentration and that the final values of intensity of the gels of different concentrations tend to increase more rapidly than the concentration. The rapid increase of intensity with concentration is more conspicuous in aluminium molybdate gels. The effect of peptising agent on the final intensity and depolarisation can be seen on comparing the corresponding values of ρ_h, ρ_v and $I_{4\pi}$ in each of the groups *a*, *b*, *c* in Table V.

TABLE V

Variation of intensity and depolarisation of Gels with Concentration

Concentration %	(a)			(b)			(c)*		
	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$
Aluminium molybdate gels set at 50° C.									
2·2	63	1·5	3·0	68	1·2	3·0	70	1·0	3·0
2·4	62	1·5	4·0	68	1·2	3·0	70	1·0	4·0
2·6	56	2·0	4·5	65	1·4	5·0	67	1·2	4·3
3·0	55	2·3	4·8	58	1·9	4·0	63	1·5	4·6
3·5	55	2·5	5·3	55	2·3	5·6	55	2·3	5·2
4·0	50	2·8	8·9	53	2·6	6·3	55	2·3	5·8
Zirconium succinate gels set at 60° C.									
1·0	55	2·3	7·0	65	1·5	3·9	65	1·5	3·9
1·1	50	2·6	8·3	63	1·6	4·3	65	1·5	3·9
1·2	50	2·6	8·3	55	2·3	7·0	60	2·0	4·8
1·3	48	2·8	9·6	53	2·4	7·8	58	2·2	6·0
1·4	40	2·9	10·0	45	2·8	9·8	50	2·6	8·2
1·5	33	4·0	11·4	40	3·1	10·0	45	2·8	9·8
Ferric succinate gels set at 50° C.									
0·3	63	5·0	1·4	68	3·7	1·2	75	1·8	0·9
0·4	63	5·0	2·0	68	3·7	1·8	73	2·2	1·3
0·5	55	7·6	2·6	65	4·4	2·1	68	3·7	1·9
0·6	50	7·8	3·0	65	4·4	2·5	68	3·7	2·3
0·7	48	8·3	3·6	60	5·3	3·3	65	4·4	2·9
0·8	40	10·3	4·3	55	7·6	3·6	65	4·4	3·3

* (*a*), (*b*) and (*c*) referred to here represent experiments in which the concentrations of the peptising agent increase from (*a*) to (*c*) as indicated in para 3.

ρ_h increases and ρ_v decreases as we go from *a* to *c*, indicating that gels containing larger excess of the peptising agent contain smaller and more symmetrical particles. Gels set at other temperatures show similar variations of intensity and depolarisation.

Changes in density scattering taking place during the sol-gel transition.— In general, I_δ-time curves may be divided into three distinct portions AB, BC and CD (Fig. 1) which show three different types of variation of intensity with time during the sol-gel transition.

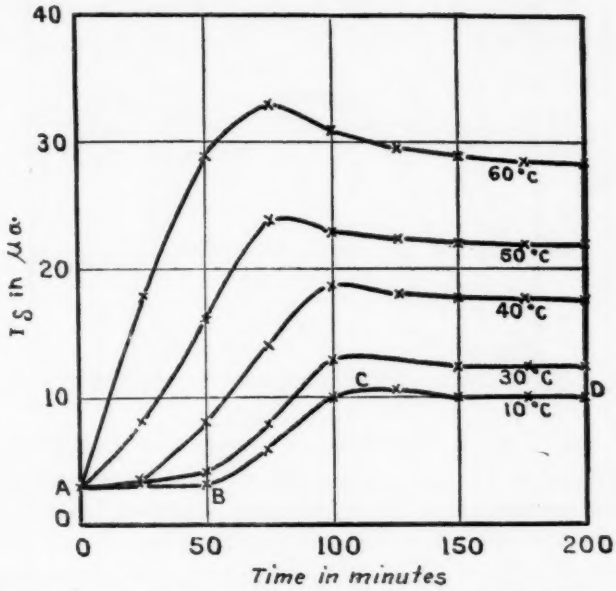

FIG. 1. I_δ-t Curves for Aluminium Molybdate. Gels of Group C. Concentration 4·0%

(i) The initial flat part AB shows that the increase in intensity of the transversely scattered light is very small in the initial stages of the sol-gel transition.

(ii) The steep part BC shows that the increase in intensity is very rapid in this time interval.

(iii) The third or flatter part CD shows that the rate of increase in intensity with time decreases rapidly again in the later stages until the intensity of scattered light remains constant after the gel has set completely. Fig. 1 shows I_δ-time curves for a 4·0% aluminium molybdate gel set at different temperatures. It is noticed from Fig. 1 that with increase in the temperature at which the sol-gel transition takes place the first part AB of the curve becomes less conspicuous and altogether vanishes at higher temperatures. In the I_δ-time curve at 60° C. the steep part BC starts right from the beginning. Fig. 2 shows I_δ-time curves for aluminium molybdate gels of different concentrations set at 60° C.

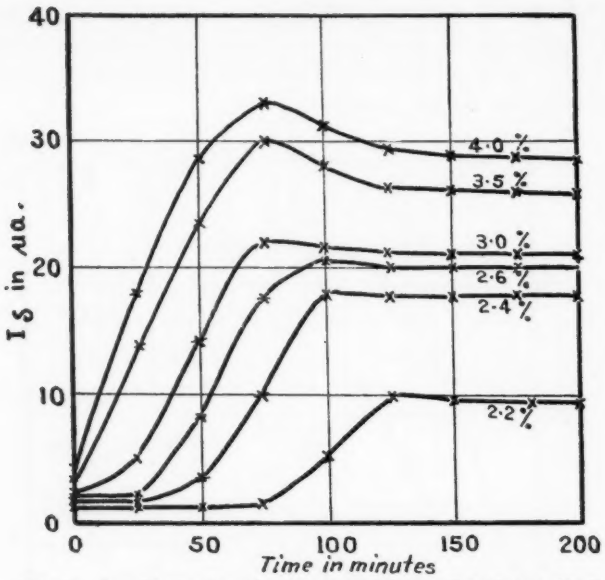

FIG. 2. I_δ-t Curves for Aluminium Molybdate Gels Set at 60° C.

On comparing the I_δ-time curves at different concentrations we notice that the first portion AB which indicates the very slow increase in intensity during the sol-gel transition, becomes less conspicuous also with increase in the concentration. Each of these curves shows the existence of a point of maximum value which is more conspicuous for gels set at higher temperatures and of higher concentrations. Fig. 3 shows the I_δ-time curves for 4·0% aluminium molybdate gels of group *a*, *b*, *c*, set at 60° C. The effect of the increase in the peptising agent is clearly seen to be to decrease the ultimate intensity of scattering.

Ageing of the gels.—The three lyophobic gels discussed in this paper show perceptible ageing effect and therefore it was possible to make a comparative study of the ageing effect in gels set under different conditions of temperature and concentration. Tables VI and VII show the intensity and depolarisation of aluminium molybdate gels of different concentrations belonging to the three different lots *a*, *b* and *c* set at 10° C. and 60° C. respectively.

From Tables VI and VII it can be seen that a slow but detectable fall in ρ_h and rise in ρ_v continues to take place for every gel indicating the growth of the size and anisotropy of the gel particles. Comparison of corresponding values of ρ_h and ρ_v in the three different groups *a*, *b* and *c*, it is noticed that increase in the peptising agent supresses the ageing effect.

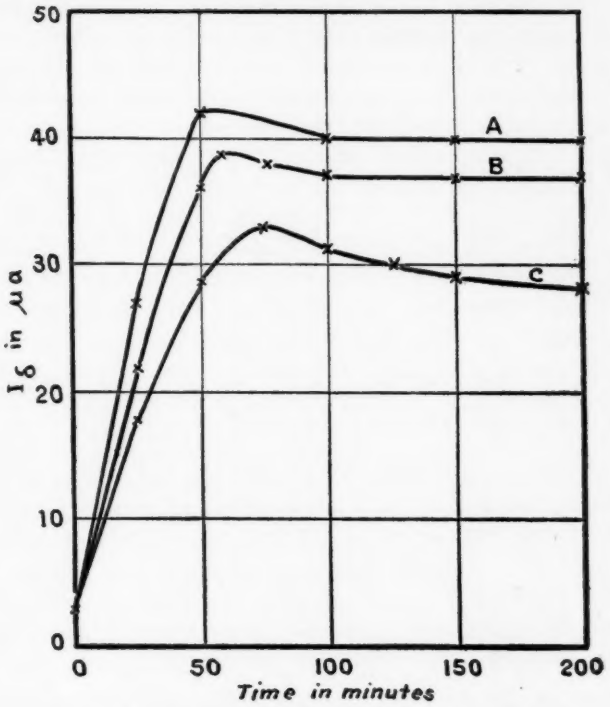

FIG. 3. I_δ-t Curves for 4·0% Aluminium Molybdate Gels

TABLE VI

Ageing of Aluminium Molybdate gels set at 10° C.

Group	Concentration %	Initial values			After 1 day			After 3 days			After 7 days		
		ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$
a	4·0	65	1·4	3·5	63	1·4	3·6	62	1·5	3·8	60	1·7	4·0
	2·2	70	1·0	2·0	70	1·0	2·0	68	1·2	2·3	68	1·3	2·5
b	4·0	65	1·3	3·5	65	1·4	3·7	63	1·5	3·9	60	1·5	4·2
	2·2	75	0·9	1·8	75	0·9	1·8	73	0·9	1·9	71	1·2	2·0
c	4·0	70	1·6	3·4	68	1·7	3·4	65	2·0	3·6	65	2·2	3·8
	2·2	80	0·9	1·7	80	0·9	1·7	80	0·9	1·7	77	1·0	1·8

TABLE VII

Ageing of Aluminium Molybdate Gels set at 60° C.

Group	Concentration %	Initial values			After 1 day			After 3 days			After 7 days		
		ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$	ρ_h %	ρ_v %	$I_{4\pi} \times 10^2$
a	4·0	40	4·8	12·4	35	5·0	12·8	33	5·3	13·2	25	5·8	13·6
	2·2	60	2·4	4·0	58	2·6	5·3	55	2·8	5·7	53	2·9	5·8
b	4·0	50	4·0	9·5	47	4·2	10·0	45	4·3	10·4	42	4·4	11·0
	2·2	65	2·2	3·7	65	2·2	3·7	66	2·1	3·5	62	2·1	6·3
c	4·0	55	3·8	9·0	53	3·9	9·2	52	3·9	9·4	50	4·0	9·6
	2·2	68	1·7	4·3	68	1·7	4·3	67	1·9	4·4	65	1·7	4·5

It is also noticed from Tables VI and VII that ageing is more pronounced in gels of higher concentrations as well as in gels set at higher concentrations. Gels of aluminium chloride set at different temperature and also those of zirconium and ferric succinate gels show similar ageing effects. A general survey of the results of the experiments on the ageing of these gels seems to indicate that the ageing may be due to the further very slow growth of the gel particles forming more anisotropic aggregates.

Variation of the viscosity of the medium during the sol-gel transition (*Qualitative study*).—The viscosity of the sol is negligible at the start and during the earlier stages of the sol-gel transition. Viscosity starts increasing rapidly only after an appreciable growth in the size of the particles has taken place, *i.e.*, nearly at the end of the steep portion BC in the I_δ-time curves. However, it increases rapidly afterwards and the gel sets completely in a few minutes. It is also noticed that the growth of the colloid particles before the increase in the viscosity starts is much more appreciable at higher temperatures. Gels prepared at higher temperatures and hence containing larger particles (as judged by lower values of ρ_h) were found to be appreciably less viscous than the corresponding ones set at low temperatures and they remain much looser even if they are cooled later to lower temperature and kept for sufficient time at the lower temperature.

6. MECHANISM OF SOL-GEL TRANSITION OF LYOPHOBIC GELS AS REVEALED BY THE PRESENT INVESTIGATION

The sol is a solid-liquid system in which the solid phase remains in the dispersion medium. The disperse phase has been shown to be always in

the colloid state and in no case molecular. In the sol state the suspended particles do not affect the free motion of the molecules of the dispersion medium materially so that the sols possess the mobility of the dispersion medium. Evidently, the stability of the sol state depends upon the extent to which the free motion of the molecules of the dispersion medium continues to remain uninfluenced by the presence of the colloid particles of the disperse phase as well as the growth of the disperse particles themselves due to collision and aggregation in the course of their Brownian motion in the liquid. The lyophobic sols are highly unstable and the aggregation of the sol particles starts soon after the sols are prepared. The instability of these sols rapidly increases with the increase in the concentration and the disperse phase rapidly precipitates out at higher concentrations. Fairly stable gels can be obtained at only very low concentrations. The initial stages of the sol-gel transition of these gels is characterised by a process of aggregation of the sol-particles with a tendency to precipitate out. The viscosity changes are inappreciable during the initial period and become evident only in the later stages. Under these circumstances a gel is obtained only if the increase in viscosity starts sufficiently early, *i.e.*, before the particles grow too big to remain in suspension. The increase in the viscosity of the medium rapidly decreases the Brownian motion of the colloid particles. The collision probability therefore decreases, preventing the further aggregation of the particles. Soon after the viscosity starts increasing the whole of the liquid state is completely bound down and the sol sets to a gel. The ultimate viscosity and the size and shape of the particles of the set gel depend upon the extent to which the particles have aggregated *before* the viscosity starts increasing. If the initial coagulation is rapid, the resulting gels are looser and contain particles of larger size. This is clearly shown by the gels prepared at higher temperatures. The Brownian motion of the particles which increases with the increase in temperature results in the increased probability of aggregation by collision and therefore gels prepared at higher temperature contain larger aggregates. It may also be noted that the clouding of the liquid phase round the colloid particles depends upon the total surface of the disperse phase and therefore with the increase in the size of the particles which results in the decrease in the total surface of the particles, the total amount of bound liquid phase also decreases giving looser and less viscous gels. The same effect is noticed with the change in the peptising agent in the sol. With the decrease in the peptising agent the collision probability increases with the result that the final gels formed contain larger aggregation.

The influence of increase in the viscosity of the sol in preventing the aggregation of the gel particles is clearly seen on comparing the size and

shape of the particles in two types gels, *viz.*, (*a*) a gel which is completely set at a lower temperature and then raised to a higher temperature and (*b*) a gel which has been prepared by carrying out the sol-gel transition at higher temperature itself. It is clearly seen that the high viscosity of the set medium does not allow appreciable growth of the gel particles and therefore the particles of the former type are much smaller than the latter. As the affinity of the dispersion medium to the disperse phase decreases, the range of concentration and temperature over which clear gels can be obtained rapidly decreases. This is evidently due to the fact that the increase in their viscosity being relatively smaller the initial growth of the particles takes place to a greater extent before it is arrested by the later increase in the viscosity. The above results therefore show that the marked turbidity of the lyophobic gels is due to the tendency of the solid phase to precipitate out so that stable gels can be obtained only by reducing the initial precipitation tendency to a minimum.

Ageing has been shown to be due to the further *very slow* aggregation of the particles in a highly viscous medium, *i.e.*, the set gel. Marked aggregation may continue wherever the viscosity of the gel is low enough. The well-known phenomenon of syneresis is probably a consequence of the ageing phenomenon. The decrease in the total surface area caused by the increase in the size of the colloid particles may let free some of the dispersion liquid clouding over the particles allowing it to separate out from the set gel.

SUMMARY

A detailed investigation on the sol-gel transition of three lyophobic gels, *viz.*, Aluminium Molybdate, Zirconium and Ferric Succinate gels, has been made by using the R. S. Krishnan colloid optical technique. Mechanism of the sol-gel transition and the various processes leading to the growth of the colloid particles as revealed by the above investigations have been discussed at length.

7. ACKNOWLEDGEMENTS

The author takes this opportunity to express his deep gratitude to Dr. L. A. Ramdas for suggesting the problem, guidance and facilities during the course of these investigations.

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RANEY NICKEL REDUCTIONS

Part III. Reduction of Anthraquinone and Its Derivatives

By V. Ramanathan, B. D. Tilak, F.A.Sc. and K. Venkataraman, F.A.Sc.
(*Department of Chemical Technology, University of Bombay*)

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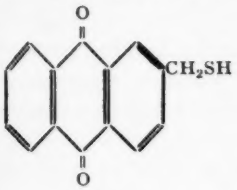
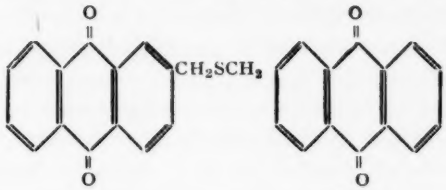
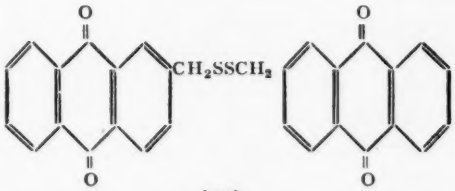
It was reported earlier that the desulphurization of Cibanone Yellow R by treatment with Raney nickel gave a difficultly separable mixture of several substances,[1] which apparently resulted from the reduction of 2-methylanthraquinone. It was necessary, therefore, to effect the desulphurization of the dye under conditions which would, if possible, leave the 2-methylanthraquinone residues in the dye unaffected after removal of sulphur and also to examine the products of the Raney nickel reduction of anthraquinone and some of its derivatives. With these objects in view the reduction of 2-methylanthraquinone, 2-mercaptomethylanthraquinone (I), *bis*-2-anthraquinonylmethyl sulphide (II) and *bis*-2-anthraquinonylmethyl disulphide (III),



(I)



(II)



(III)

which may be intermediates in the formation of the dye, was studied. A comparative study of the reduction of anthraquinone was also carried out.

Anthraquinone and 2-methylanthraquinone have been converted to different hydro derivatives by the action of hydrogen in presence of metal catalysts, such as platinum in glacial acetic acid[2] and nickel in alcohol under pressure.[3] Raney nickel has been used in aqueous alkali,[4] in dioxane,[5]

and in alcohol[6, 7] at atmospheric pressure. Papa[8] has effected desulphurizations in alkaline solutions by the addition of Raney alloy; under those conditions it was expected that Cibanone Yellow R, which is sparingly soluble in organic solvents, would vat and dissolve and then undergo desulphurization smoothly. The reduction of 2-methylanthraquinone was therefore studied particularly under these conditions.

Reduction of 2-methylanthraquinone with Raney alloy in aqueous alkali led to several derivatives of 2-methylanthraquinone. Using 2-methylanthraquinone (1 part) and Raney alloy (4 parts) for 10 hours, 5 crystalline products were obtained, which analysed for dihydro- (m.p. 126–7°), tetrahydro- (m.p. 170–1°), and octahydromethylanthraquinone (m.p. 136°, m.p. 146° and m.p. 163–4°). Raney alloy (2·5 parts) for 1 hour gave tetrahydro-2-methylanthraquinone (m.p. 170–1° identical with the tetrahydro derivative mentioned above). One part of Raney alloy for 1 hour gave some unreacted 2-methylanthraquinone (0·35 part), together with reduction products. Reduction of anthraquinone (1 part) with Raney alloy (2 parts) for 2 hours gave 1:2:3:4-tetrahydroanthraquinone.

The constitution of the reduction products was determined by oxidative degradation. 1:2:3:4-Tetrahydroanthraquinone on oxidation with potassium permanganate in acetone gave a mixture of phthalic and adipic acids, which were separated by taking advantage of the insolubility of the lead salt of phthalic acid in glacial acetic acid.[9] Oxidation of tetrahydro-2-methylanthraquinone under similar conditions gave 4-methylphthalic acid and adipic acid, indicating that the tetrahydro derivative is 1:2:3:4-tetrahydro-6-methylanthraquinone. Reductive acetylation gave 9:10-diacetoxy-1:2:3:4-tetrahydro-6-methylanthracene.

Fusion of tetrahydroanthraquinone derivatives with caustic potash was not useful for determining their constitution, since tetrahydrobenzoic acids were not isolable. When tetrahydroanthraquinone was fused with caustic potash, anthraquinone was mainly formed, together with a small amount of benzoic acid. Dehydrogenation appeared to precede degradation.

In the course of their work on the constitution of vitamins K_1 and K_2, Fieser *et al.* synthesized several 2:3-dialkyl-1:4-naphthoquinones.[10] They found a close correspondence between the spectra of the vitamins and the synthetic naphthoquinones,[11, 12, 13] as well as their physiological and antihemorrhagic activity. Since 1:2:3:4-tetrahydroanthraquinone is structurally allied to 2:3-dialkyl-1:4-naphthoquinones and gives an absorption spectrum (Fig. 1) closely resembling the spectra of the naphthoquinones, it is likely to possess antihemorrhagic activity. The bathochromic shift

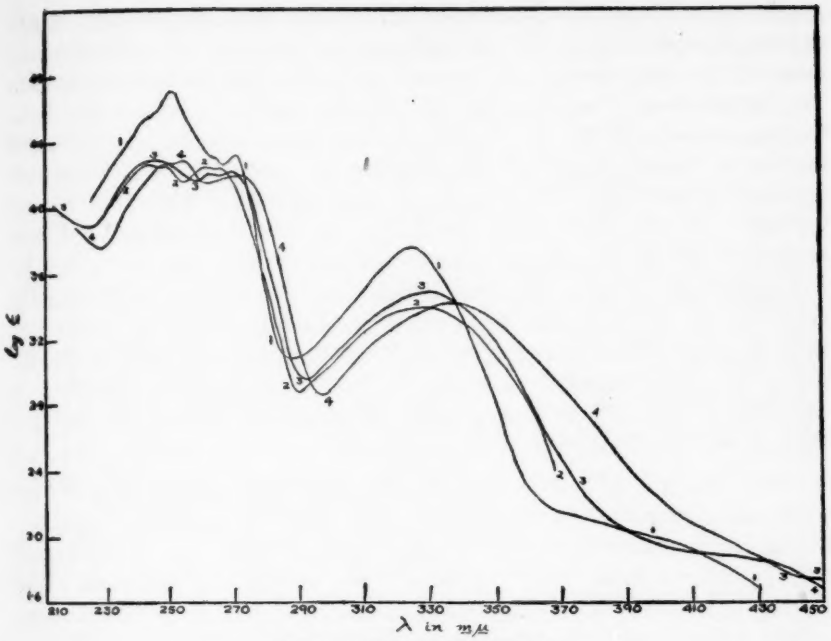


FIG. 1. Absorption spectrum of

(1) Anthraquinone*; (2) 2:3:-dimethy 1-1:4-naphtho-quinone*; (3) 1:2:3:4:-tetrahydro-anthraquinone, and (4) 1:2:3:4-tetrahydro-6-methylanthraquinone in ethanol.

(* Redrawn from Morton and Earlam, *J. Chem. Soc.*, 1941, 159; Fieser *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 2206.)

in the spectrum of 1:2:3:4-tetrahydromethylanthraquinone shows that the methyl group is present in the unreduced benzene ring. The reduction of the unsubstituted ring in 2-methylanthraquinone would appear to be in agreement with the observation of Stork[14] that " in a polycyclic aromatic compound that ring will become reduced, the reduction of which will result in the smallest loss of resonance energy by the system".

Having arrived at a mild reduction procedure whereby at least a part of the 2-methylanthraquinone was left unreduced, the desulphurization of the simple sulphur-containing derivatives (I, II and III) of 2-methylanthraquinone was next examined. The exocyclic sulphur in these compounds was expected to poison part of the catalyst during reduction and thus prevent the reduction of the 2-methylanthraquinone residue. 2-Mercaptomethylanthraquinone (I) gave a mixture of 2-methylanthraquinone, 2-hydroxymethylanthraquinone, anthraquinone-2-carboxylic acid, and *bis*-2-anthraquinonylmethyl sulphide (II). *Bis*-2-anthraquinonylmethyl sulphide (II) gave

a mixture of 2-methylanthraquinone and traces of Anthraflavone. *Bis*-2-anthraquinonylmethyl disulphide (III) gave a mixture of 2-methylanthraquinone, 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid. The preparation of compounds (I), (II) and (III), carried out by S. P. Chandavarkar will be reported separately. Desulphurization of benzyl mercaptan and di-*p*-tolyl sulphide under similar conditions has been studied by Papa, who obtained toluene as the only product.[8] The behaviour of the anthraquinone derivatives is thus distinctive. The isolation of 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid, in addition to 2-methylanthraquinone, from the desulphurization products of (I) and (III) is of interest. In the desulphurization of (II), in addition to 2-methylanthraquinone, Anthraflavone was isolated in small quantities. In the desulphurization of (I), (II) was obtained as one of the products; the formation of a compound with lower sulphur content indicates the poisoning effect of the thiol group on the nickel catalyst.[15]

The reduction of α: β-*bis*-2-anthraquinonylethylene (Anthraflavone) with Raney alloy gave a mixture of products from which a compound analysing for decahydroanthraflavone and a small quantity of 1:2:3:4-tetrahydro-6-methylanthraquinone were isolated. Part of the Anthraflavone thus cleaved at the ethylene bridge during reduction. Fission of the carbon-carbon linkage has been reported by Snyder and Cannon who obtained methane and ethane by the Raney nickel reduction of ethers of ethylenedithiol.[16] Earlier we have reported that reduction of thioindigo with Raney alloy yields benzoic acid among other products.[17] In view of the fact that the reduction of 2-methylanthraquinone under mild conditions yields 1:2:3:4-tetrahydro-6-methylanthraquinone, it is likely that the unsubstituted benzene rings and the ethylene link in Anthraflavone are reduced and that the decahydroanthraflavone mentioned earlier is constituted as α: β-6:6′-*bis*-(1:2:3:4-tetrahydroanthraquinonyl) ethane.

Another approach to the determination of the nature of the desulphurization products obtained from Cibanone Yellow R would be to dehydrogenate the reduced anthraquinone derivatives to anthraquinone derivatives, which may be more amenable to separation. Dehydrogenation of 1:2:3:4-tetrahydroanthraquinone and 1:2:3:4-tetrahydro-6-methylanthraquinone was therefore studied. The conversion of anthrone to anthraquinone in 80–90% yield by passage of a benzene solution through an alumina-Celite column has been reported.[18] We have now found that 1:2:3:4-tetrahydroanthraquinone and its 6-methyl derivative are converted to the corresponding anthraquinones in 95% yield, when a hexane solution is passed

through a column of alumina (Brockmann standard activity I). The tetrahydro derivatives were also dehydrogenated by shaking a hexane solution with excess of alumina. Alumina of lower activity was either ineffective or effected partial dehydrogenation. That light did not play a part in the dehydrogenation was shown by carrying out the reaction in the dark. Solvents more polar than hexane were unsuitable for the dehydrogenation, which also did not take place when other adsorbents such as Fuller's earth and calcium sulphate were used.

Dehydrogenation of 1:2:3:4-tetrahydroanthraquinone to anthraquinone by hot aniline and cyclohexylamine,[19] by sulphuric acid, and by bromination of the hydrogenated nucleus and subsequent loss of hydrogen bromide[3] have been reported. It has now been found that alkali fusion gave the dehydrogenated product together with a trace of benzoic acid. Tetrahydroanthraquinone was also dehydrogenated by boiling pyridine in good yield. Dehydrogenation by means of chloranil in boiling xylene was unsuccessful. Treatment of the reduced anthraquinones with sulphur at 200° gave the parent anthraquinones. Excellent yields of the anthraquinones were obtained when tetrahydroanthraquinone derivatives were treated with iodine and sodium acetate in boiling nitrobenzene. Iodine and sodium acetate in alcoholic solution has been used for dehydrogenation purposes.[20] This method, however, failed with the reduced anthraquinones. Iodine has been used for aromatization at high temperatures, but the reaction was accompanied by partial dehydrogenation condensation.[21] This is eliminated by the use of sodium acetate as acid-binding agent and nitrobenzene as solvent. Treatment of decahydroanthraflavone with iodine under these conditions gave α:β-*bis*-2-anthraquinonylethane (dihydroanthraflavone). The latter product was not further dehydrogenated by iodine in nitrobenzene, but treatment with excess of selenium dioxide in boiling nitrobenzene yielded Anthraflavone. The action of selenium dioxide on dibenzyl has been shown to result in benzene, benzaldehyde, stilbene and benzil, or a mixture of stilbene and benzil, depending on the conditions employed.[22] In the case of Anthraflavone oxidation to the diketo derivative or fission of the carbon-carbon linkage does not occur in spite of the use of a large excess of selenium dioxide. When a mixture of 1:2:3:4-tetrahydroanthraquinone (1 mol.) and selenium dioxide (1·1 mol.) was heated at 170°, the major products were anthraquinone and α-hydroxyanthraquinone. With excess of selenium dioxide (4 mol.) tetrahydroanthraquinone gave quinizarin as one of the products. The action of selenium dioxide on reduced 2-methylanthraquinones is under investigation. By analogy with the formation of hydroxyanthraquinone derivatives, reduced 2-methylanthraquinone derivatives may lead

to similar hydroxy derivatives, which are of interest because of their occurrence in nature.

EXPERIMENTAL

Reduction of anthraquinone

A suspension of anthraquinone (10 g.) in 10% caustic soda solution (300 c.c.) was heated to 90° and Raney alloy (20 g.) was added in small portions under stirring. After the addition was complete, the reaction mixture was further heated on a boiling water-bath for 1 hour. Nickel was filtered off, washed thoroughly with water, acidified, and again filtered, washed and dried. The residue on extraction with benzene gave a brown solid (2·3 g.). The deep red alkaline filtrate on passing air gave a yellow precipitate (7·1 g.). The two products were combined and crystallized successively from alcohol and aqueous acetic acid. The yellow needles (7 g.) had m.p. 158–9° (Found: C, 79·0; H, 5·4. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·6%). The m.p. of 1:2:3:4-tetrahydroanthraquinone cited by Skita[2] is 159°.

Reduction of 2-methylanthraquinone

Method 1.—A suspension of 2-methylanthraquinone (10 g.) in 10% caustic soda solution (300 c.c.) was heated on a water-bath, and Raney alloy (40 g.) was added in small portions under vigorous stirring. The mixture was heated for 10 hours and filtered.

The nickel residue was washed and then treated with concentrated hydrochloric acid. After keeping overnight, the mixture was filtered, washed and dried and the residue extracted with chloroform in a Soxhlet for 2 days. The extract gave a brown solid (4·3 g.) which was chromatographed on alumina, using chloroform as the solvent. Four zones separated: (1) red, strongly adsorbed; (2) negligibly small yellow zone; (3) brown, eluted with chloroform; (4) yellow, eluted with chloroform. The chloroform eluant from the fourth (bottom) zone gave a yellow substance which after repeated crystallization from alcohol was obtained as yellow needles, m.p. 146° (Found: C, 78·5; H, 6·9. $C_{15}H_{18}O_2$ requires C, 78·3; H, 7·8%. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·0%). Concentration of the mother-liquor led to yellow needles (A), which on repeated crystallization from alcohol, had m.p. 136° (Found: C, 78·5; H, 6·9%). The crude material obtained from zone (4) dissolved in alkaline hydrosulphite giving a red solution. Reoxidation of the vat gave a pale yellow substance which, after 3 crystallizations from methanol, was obtained as yellow needles (B), m.p. 161° (Found: C, 78·2; H, 7·0%). Concentration of the methanolic mother liquor gave a product which, after 4 crystallizations, was obtained as needles,

m.p. 136°, undepressed when mixed with (A). Evaporation of the chloroform eluant from the third zone gave an oil which dissolved in hot aqueous alkali with a red colour and coupled with diazonium salts. The alumina column was pushed out and the first 2 zones were separated by cutting the column. Extraction of the first zone with alcohol containing a few drops of hydrochloric acid yielded a brown solution of a phenolic substance, which gave a dark brown colour with ferric chloride and coupled with diazonium salts.

The dark red alkaline filtrate, on aeration for 1 hour, gave a yellow solid (C) (3·2 g.). On further aeration a brown solid (D) separated (1·7 g.). Substance (C) was dissolved in chloroform and chromatographed on alumina, when 5 zones separated. The eluant from the yellow zone at the bottom percolate gave a substance which, on crystallization from alcohol and then from methanol, was obtained as yellow needles (E), m.p. 170–1°, depressed when mixed with 2-methylanthraquinone (Found: C, 79·8; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·2%). The eluant from the next zone yielded yellow needles, m.p. 163–4°, identical with compound (B) (Found: C, 78·1; H, 7·2%). The strongly held chocolate and pink zones at the top and the middle dark brown zone did not lead to crystalline material.

When substance (D) was chromatographed on alumina using chloroform as solvent, the major component was eluted first; three crystallizations from methanol gave yellow needles, m.p. 126–7° (Found: C, 80·1; H, 5·6. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·3%).

Thus 2-methylanthraquinone, on reduction by method 1 gave 3 compounds, m.p. 136°, 146°, 163–4°, analysing for octahydro-2-methylanthraquinone, a compound (E), m.p. 170–1° analysing for tetrahydro-2-methylanthraquinone, and a fifth product, m.p. 126–7°, analysing for dihydro-2-methylanthraquinone. Except the tetrahydro derivative, the other hydrogenation products turned dark red in colour and the m.ps. changed on storage.

Method 2.—2-Methylanthraquinone (10 g.) was treated with Raney alloy (25 g.) and 10% sodium hydroxide solution (300 c.c.) as above for 1 hour and the mixture filtered. Aeration of the red alkaline filtrate precipitated a yellow solid (8·2 g.), which crystallized from acetic acid in yellow needles (5 g.), m.p. 170–1°, identical with the tetrahydro derivative (E).

Method (3).—2-Methylanthraquinone (10 g.) was treated with Raney alloy (10 g.) and 10% sodium hydroxide solution (300 c.c.) as above for 1 hour. Aeration of the filtrate and crystallization of the precipitate from

alcohol gave a 35% recovery of unchanged 2-methylanthraquinone, m.p. 172°.

Oxidation of 1:2:3:4-*tetrahydroanthraquinone*

Tetrahydroanthraquinone (0·2 g.) was dissolved in acetone (25 c.c.) at 25° and powdered potassium permanganate was added slowly till a pink colour remained; the mixture was then refluxed, and since the pink colour was discharged more permanganate was added till a faint pink persisted. The total permanganate added was 0·7 g. The heating was continued for 2 hours. After distilling off acetone, the residue was extracted with hot water and the extract acidified with hydrochloric acid and evaporated to dryness. Ether extraction of the residue and evaporation of ether led to a sticky yellow substance (0·25 g.) which was dissolved in glacial acetic acid (15 c.c.) and warmed to 60°. A solution of lead acetate trihydrate (0·5 g.) in glacial acetic acid (2 c.c.) was added. The turbid solution was left overnight, and filtered from the precipitate (A). The filtrate was evaporated, acidified with dilute hydrochloric acid, evaporated to dryness, and the residue extracted with ether. The ether extract gave a yellow substance, which was triturated with chloroform and filtered. The residue crystallized from concentrated nitric acid in colourless prisms (0·07 g.), m.p. 151°, identified as adipic acid.

The precipitate (A) was treated with dilute hydrochloric acid, evaporated to dryness and extracted with ether. The ether extract gave colourless needles (0·11 g.), m.p. 199–200° (dec.). On refluxing with acetyl chloride for 1 hour and evaporating, the residue crystallized from hexane in colourless needles, m.p. 131°, identified as phthalic anhydride.

Oxidation of tetrahydromethylanthraquinone

Oxidation of tetrahydromethylanthraquinone (0·2 g.) as above gave adipic acid (0·05 g.). A second acid was formed, which gave a lead salt insoluble in glacial acetic acid. After recovery from the lead salt and crystallization from benzene, the microcrystalline powder had m.p. 147° (Found: C, 60·5; H, 4·4. Calc. for $C_9H_8O_4$: C, 60·0; H, 4·4%). The acid appeared to be 4-methylphthalic acid, for which the m.p. quoted in the literature is 152°.[23] This was confirmed by conversion into the anhydride, m.p. 92°.

Reductive acetylation of tetrahydromethylanthraquinone

Tetrahydromethylanthraquinone (0·4 g.), acetic anhydride (5 c.c.), zinc dust (0·8 g.) and pyridine (5 drops) were refluxed for 2 hours. On pouring

into ice and hydrochloric acid, the colourless precipitate (0·4 g.) was collected, washed, dried, dissolved in carbon tetrachloride and chromatographed on alumina. The colourless percolate gave a product which crystallized from alcohol in needles, m.p. 155° (Found: C, 72·6; H, 6·6. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%).

Alkali fusion of tetrahydroanthraquinone

Tetrahydroanthraquinone (0·5 g.) was slowly added to molten caustic potash (5·0 g.) under stirring at 200°, and the mixture was stirred for 3 hours at 210°. After cooling the melt was extracted with water and acidified with hydrochloric acid. The precipitate (0·47 g.) proved to be anthraquinone. Ether extraction of the filtrate gave a colourless product (0·02 g.), most of which was soluble in chloroform. The chloroform-insoluble residue gave the fluorescein test and was apparently phthalic acid. The chloroform-soluble portion crystallized from water in needles, m.p. 121°, undepressed when mixed with benzoic acid.

Desulphurization of 2-mercaptomethylanthraquinone

The thiol (5 g.) was heated with Raney alloy (5 g.) in 10% caustic soda solution (150 c.c.) on a water-bath for 1 hour. Filtration from nickel and aeration of the filtrate gave a reddish brown, sulphur-free precipitate (1·5 g.). The substance was extracted with alcohol (60 c.c.) and the insoluble residue (A) and the extract worked up separately. The latter was evaporated to dryness, and the residue was dissolved in acetone and chromatographed on alumina. The first percolate contained the major fraction (0·26 g.) which separated from alcohol as a yellow crystalline powder, m.p. 182° (Found: C, 75·2; H, 4·5. Calc. for $C_{15}H_{10}O_3$: C, 75·6; H, 4·2%). The m.p. and elementary analysis of the product are in agreement with those of 2-hydroxymethylanthraquinone, m.p. 183°.[24]

The residue (A) crystallized from acetic acid in pale yellow needles (0·57 g.), m.p. 285–6°; undepressed when mixed with anthraquinone-2-carboxylic acid.

The nickel residue after treatment with hydrochloric acid was extracted with benzene in a Soxhlet for 3 days. The benzene extract gave a product (2·45 g.) containing sulphur. Extraction with alcohol (75 c.c.) effected a fractionation into an insoluble substance (B) and an alcoholic extract. The alcohol-soluble substance was dissolved in carbon tetrachloride and chromatographed on alumina, using chloroform as eluant. The first percolate gave a yellow compound (0·57 g.), which crystallized from alcohol in pale yellow needles, m.p. 172° undepressed when mixed with 2-methylanthraquinone.

The alcohol-insoluble residue (B) crystallized from acetic acid in small needles (0·87 g.), m.p. 244°, and was identified as *bis*-2-anthraquinonylmethyl sulphide by a mixed m.p.

Desulphurization of bis-2-*anthraquinonylmethyl sulphide*

The sulphide (5 g.) was treated with Raney alloy (5 g.) in 10% aqueous caustic soda solution (150 c.c.) as above for 1 hour. The reaction mixture was filtered and the red alkaline filtrate on passing air gave a yellow product (3·25 g.). Extraction with alcohol (225 c.c.) and concentration of the extract gave a product (2·5 g.), m.p. 171°; undepressed when mixed with 2-methylanthraquinone.

The alcohol-insoluble residue (0·22 g.) contained sulphur. On extraction with acetic acid a sulphur-free residue was obtained which crystallized from nitrobenzene in yellow needles, m.p. 434°, undepressed when mixed with Anthraflavone.

The nickel residue, after acidification, washing, drying and Soxhlet extraction with benzene, gave a product, which on chromatographic purification on alumina, led to 2-methylanthraquinone (0·75 g.).

Desulphurization of bis-2-*anthraquinonylmethyl disulphide*

The disulphide (5 g.) was treated with Raney alloy (5 g.) and 10% caustic soda solution (150 c.c.) on a water-bath for 1 hour. The greenish alkaline filtrate on aeration gave a brownish sulphur-free product (1·85 g.). On extraction with alcohol (50 c.c.) and chromatographic purification of the alcohol-soluble portion, 2-hydroxymethylanthraquinone (0·4 g.), m.p. 182°, was obtained. The alcohol-insoluble portion crystallized from acetic acid in needles (0·8 g.), m.p. 285–6°, undepressed when mixed with anthraquinone-2-carboxylic acid.

The nickel residue, after deactivation as usual and Soxhlet extraction with benzene, gave a sulphur-free sticky substance (1·55 g.). After chromatographing twice on alumina, using carbon tetrachloride as solvent and crystallizing from alcohol, 2-methylanthraquinone (0·87 g.) was obtained.

Reduction of Anthraflavone

Anthraflavone (5 g.) was dissolved in concentrated sulphuric acid and reprecipitated with water. The precipitate was filtered, washed free from acid, and the wet cake suspended in 10% caustic soda solution (150 c.c.). The mixture was treated with Raney alloy (15 g.) as above for 1 hour. The brownish red alkaline filtrate, on aeration, gave a yellow product (A) (2·65 g.). The alkaline solution after separation of (A) was poured into excess of

concentrated hydrochloric acid and the dark brown precipitate (B) was collected. Substance (A) was extracted with alcohol (100 c.c.) and product obtained from the alcoholic extraction was dissolved in carbon tetrachloride and chromatographed on alumina. The first fraction on concentration gave yellow needles, m.p. 170°, undepressed when mixed with 1:2:3:4-tetrahydro-6-methylanthraquinone. The major component was a brown uncrystallizable substance.

The alcohol-insoluble residue (1·6 g.) was dissolved in pyridine and chromatographed on alumina, using carbon tetrachloride as the eluant. The major fraction, which was eluted first, crystallized from acetic acid in yellow plates, m.p. 254° (Found: C, 79·3; H, 5·9. Decahydroanthraflavone, $C_{30}H_{36}O_4$ requires C, 80·0; H, 5·8%). Substance (B) was extracted with aqueous sodium bicarbonate in which the major part went into solution. The extract on acidification gave a brown precipitate which could not be crystallized. Likewise, no crystalline material was recoverable from the nickel residue.

Dehydrogenation of tetrahydroanthraquinone by activated alumina

Method 1.—Tetrahydroanthraquinone (0·2 g.) was dissolved in hexane (50 c.c.) and passed through a column (25 cm. long and 1·5 cm. diameter) of alumina (35 g.; Grade I, Brockmann standard). Elution was effected with 2·5 l. of hexane. Removal of the solvent from the percolate and crystallization from acetic acid gave anthraquinone (0·16 g.), m.p. 286° and unconverted tetrahydroanthraquinone (0·03 g.), m.p. 157°.

Under similar conditions, tetrahydromethylanthraquinone gave 2-methylanthraquinone in 95% yield.

Method 2.—Tetrahydroanthraquinone (1 part) was dissolved in hexane and shaken with alumina (100 parts; Grade I, Brockmann standard) for 25 hours. Extraction of the alumina with alcohol gave anthraquinone. Tetrahydromethylanthraquione was similarly converted to 2-methylanthraquinone.

These treatments were repeated with the exclusion of light, but the same results were obtained.

Dehydrogenation of tetrahydroanthraquinone with pyridine

Tetrahydroanthraquinone (0·05 g.) was refluxed with pyridine (5 c.c.) for 24 hours. The yellow solution slowly turned dark brown. On pouring into ice and hydrochloric acid, the precipitate (0·045 g.) had m.p. 279–80° and was identified as anthraquinone.

Tetrahydromethylanthraquinone on similar treatment gave 2-methylanthraquinone.

Action of chloranil on tetrahydroanthraquinone

Tetrahydroanthraquinone (0·5 g.) and chloranil (1·25 g.) were added to sulphur-free xylene (40 c.c.) and refluxed for 20 hours. The mixture was then cooled, diluted with ether (40 c.c.) and filtered. The filtrate was extracted with 5% caustic soda solution (200 c.c.). The xylene layer was warmed to expel the ether and the xylene steam distilled. The residual solid crystallized from aqueous acetic acid in needles (0·35 g.), m.p. 158°, undepressed when mixed with tetrahydroanthraquinone.

Dehydrogenation of tetrahydroanthraquinone by sulphur

Tetrahydroanthraquinone (0·5 g.) was mixed with sulphur (0·22 g.) and heated at 200° for 3 hours. The mixture was then extracted with sodium sulphide solution to remove the excess of sulphur and then with acetic acid, some resinous material being left behind. The acetic acid extract gave a yellow substance (0·2 g.) on evaporation and it crystallized from alcohol in yellow needles, m.p. 278°, undepressed when mixed with anthraquinone.

Dehydrogenation of tetrahydromethylanthraquinone by sulphur

Tetrahydromethylanthraquinone (0·5 g.) was mixed with sulphur (0·42 g.) and heated at 200° for 5 hours when the evolution of hydrogen sulphide was nearly complete. The mixture was extracted with sodium sulphide solution to remove excess of sulphur and then with alcohol. The alcoholic solution on evaporation gave a yellow substance (0·22 g.), which was chromatographed on alumina using chloroform as solvent. 2-Methylanthraquinone (0·2 g.), m.p. 171–2°, was isolated as the main product.

Dehydrogenation of tetrahydroanthraquinone by iodine

Tetrahydroanthraquinone (0·5 g.), fused sodium acetate (2·0 g.) and iodine (1·5 g.) were refluxed with nitrobenzene (25 c.c.) for 6 hours. The solvent was steam distilled and the residue was treated with aqueous sodium thiosulphate solution to remove traces of unreacted iodine. On crystallization from alcohol, anthraquinone (0·4 g.) was obtained.

Dehydrogenation of tetrahydromethylanthraquinone by iodine

Tetrahydromethylanthraquinone (0·5 g.), fused sodium acetate (2·0 g.) and iodine (2·3 g.) were refluxed with nitrobenzene (25 c.c.) for 6 hours. On working up as described above, 2-methylanthraquinone (0·35 g.) was obtained.

Dehydrogenation of decahydroanthraflavone by iodine

Decahydroanthraflavone (0·38 g.), sodium acetate (2 g.) and iodine (1·35 g.) were refluxed with nitrobenzene (20 c.c.) for 6 hours. Nitrobenzene was removed by steam distillation and the residue was crystallised from *o*-dichlorobenzene in needles (0·28 g.), m.p. 330°, undepressed when mixed with dihydroanthraflavone.

Dehydrogenation of dihydroanthraflavone by selenium dioxide

Dihydroanthraflavone (0·1 g.) and selenium dioxide (0·4 g.) were refluxed with nitrobenzene (10 c.c.) for 7 hours and filtered hot. The filtrate on cooling gave a substance, which crystallized from nitrobenzene in yellow needles (0·08 g.), m.p. 430–1°, identified as Anthraflavone by m.p. and mixed m.p. and the violet colouration with sulphuric acid.

Action of selenium dioxide on tetrahydroanthraquinone

Method 1.—Tetrahydroanthraquinone (0·5 g.; 1 mol) and selenium dioxide (1·05 g.; 4 mol.) were thoroughly mixed and heated in a test tube fitted with an air condenser. The mixture was slowly heated to 170° and maintained at this temperature for 2 hours. The reaction mixture was extracted repeatedly with alcohol. The alcoholic extract was taken down to dryness and extracted with 10% caustic soda solution. The minute amount of alkali-insoluble matter was not examined further. The violet alkaline extract on acidification gave a red solid which was sublimed at 200°/3 mm. The sublimate was dissolved in alcohol and the solution, on leaving in the refrigerator, slowly deposited a red crystalline product, m.p. 195–6°, undepressed when mixed with quinizarin. The mother liquor was evaporated and the residue was dissolved in acetone and chromatographed on heavy magnesium carbonate. An upper pink zone and a lower orange zone separated. The zones were cut out and treated with hydrochloric acid and ether. The ether extract from pink zone led to quinizarin, and orange band yielded α-hydroxyanthraquinone.

Method 2.—A mixture of tetrahydroanthraquinone (0·5 g.; 1 mol.) and selenium dioxide (0·29 g.; 1·1 mol.) was heated and worked up as above. The major product was insoluble in aqueous caustic soda; this was chromatographed on alumina using chloroform as solvent. A yellow percolate and an orange zone on the alumina were obtained. The percolate on evaporation gave anthraquinone. The strongly adsorbed substance was isolated by extraction of the alumina with alcohol containing a few drops of hydrochloric acid. The yellow solution gave yellow needles, which on recrystal-

lization from alcohol had m.p. 191°, undepressed when mixed with α-hydroxyanthraquinone.

SUMMARY

Reduction of anthraquinone, 2-methylanthraquinone, 2-mercaptomethylanthraquinone (I), *bis*-2-anthraquinonylmethyl sulphide (II) and *bis*-2-anthraquinonylmethyl disulphide (III) by Raney alloy in aqueous alkaline solution was studied. Anthraquinone gave 1:2:3:4-tetrahydroanthraquinone. When 2-methylanthraquinone was reduced with varying amounts of Raney alloy, several hydro derivatives of 2-methylanthraquinone were obtained. One was 1:2:3:4-tetrahydro-6-methylanthraquinone, the constitution of which was proved by oxidation to adipic and 4-methylphthalic acids. Desulphurization of (I) gave 2-methylanthraquinone, 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid; (II) gave 2-methylanthraquinone and traces of Anthraflavone; and (III) gave 2-methylanthraquinone, 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid. Anthraflavone gave decahydroanthraflavone as the major product and a small amount of 1:2:3:4-tetrahydro-6-methylanthraquinone.

Dehydrogenation of tetrahydro- and tetrahydromethylanthraquinones to the parent compounds was effected by several methods including treatment with iodine and sodium acetate in nitrobenzene and the action of activated alumina on a hexane solution. Treatment of tetrahydroanthraquinone with selenium dioxide at 170° gave a mixture of anthraquinone, α-hydroxyanthraquinone and quinizarin. Decahydroanthraflavone was dehydrogenated in two steps to Anthraflavone.

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THE DIPOLE MOMENTS OF FUROIN AND HYDROFURAMIDE*

By Sundaresa Soundararajan‡ and S. V. Anantakrishnan, F.A.Sc.
(Department of Chemistry, Madras Christian College, Tambaram)

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In spite of the long history of furan compounds the structure of furan derivatives has generally presented difficulties. Their chemical behaviour is determined jointly by the nucleus and by the groups attached thereto. The best known member of the series is the aldehyde furfural, whose reactions are analagous to those of benzaldehyde. Thus with potassium cyanide as catalyst, it forms furoin, while condensation with ammonia gives hydrofuramide the furan analog of hydrobenzamide.

These two compounds are particularly interesting because of the stereochemical problems presented by such multinuclear systems. Further, the latter compound has an added interest in the computation of moments because of the presence of the ammono aldehyde group and a N-C-N bond. The presence of an asymmetric carbon atom in furoin suggests the existence of optically active forms but the presence of a carbonyl group at the adjacent carbon atom as well as the heterocyclic ring should facilitate ready recemisation and very dilute solutions may be expected to show interesting properties. The spatial disposition of the hydroxyl group is of importance in giving us information as to the likelihood of hydrogen bonding as well. Also the presence of a heteroatom in the ring makes the direction of ring moment an important factor in determining the total moment of the molecule. This factor assumes an even greater significance in the case of hydrofuramide. The present work on dipole moments of these two compounds was undertaken with a view to throw some light on the spatial configurations of these molecules.

Experimental

'Analar' benzene was repeatedly shaken with concentrated sulphuric acid, washed with water, treated with a solution of caustic soda, washed again with water, dried over anhydrous calcium chloride and distilled.

* Based on thesis of S. S. approved for the M.Sc. degree of Madras University.

‡ Present address: Department of General Chemistry, Indian Institute of Science, Bangalore-3.

The middle fraction obtained by fractional distillation was frozen out and finally stored over sodium wire which retained its brightness.

Furoin was prepared by the standard procedure for benzoin condensations.[1] After decolourisation with animal charcoal it was recrystallised twice from methyl alcohol and finally from a mixture of toluene and alcohol, m.p. 135° C.

Hydrofuramide was obtained by allowing freshly distilled furfural to react with five times the quantity of concentrated ammonia solution. After three hours, the separation of the product was complete. The product was recrystallised thrice from alcohol, m.p. 117° C.

Measurements of dielectric constants were made using an A.C. mains operated heterodyne beat apparatus similar to that of Hudson and Hobbs[6] details of which have been given earlier.[10] Densities of the dilute benzene solutions were obtained using an Ostwald Sprengel pycnometer with closed ground in caps at both ends. Refractive indices of solutions of various concentrations were measured with an Abbe refractometer. The molar refraction calculated from these measurements was compared with the value as calculated using the additivity of bond refractions.[3] The polarisation ${}_{T}P_{1}$ of the solute at infinite dilution was obtained using the mean values of the Hedestrand constants α and β.[5] The relevant data are collected together in Tables I and II below.

TABLE I

Furoin: Temp. 35° ± ·005° C.
Mol. wt. 192·16

Mole fraction	Dielectric constant ϵ	Density d	α†	β
0·0	2·25700*	·86278	..	..
0·0002337	2·26126	·86352	8·074	3·695
0·0003649	2·26407	·86396	8·606	3·764
0·0005211	2·26730	·86432	8·756	3·437
0·0008317	2·27345	·86546	8·760	3·741
		Average ..	8·550	3·659

* Extrapolated graphically to zero concentration.

α † Calculated using extrapolated benzene value: 2·2570

${}_{M}R_{D}$ calculated = 47·38 c.c.

Total polarisation = 257·34 c.c.

μ = 3·24 D

TABLE II

Hydrofuramide: Temp. 35° ± ·005° C.
Mol. wt. 268·26.

Mole fraction	Dielectric constant ϵ	Density d	α	β
0·0	2·2535	·86278		
0·001887	2·2758	·86460	5·243	1·121
0·004716	2·3011	·86760	4·481	1·186
0·006786	2·3194	·86969	4·318	1·181
0·009057	2·3419	·87207	4·335	1·160
0·010907	2·3579	·87300	4·247	1·085
		Average ..	4·525	1·147

$_{M}R_{D}$ (measured) = 70·57 c.c. Total polarisation = 214·15 c.c
$_{M}R_{E}$ (calculated) = 71·64 c.c. μ = 2·66 ± ·01 D

DISCUSSION

By comparing the observed moment of a system with a value expected for it from the known values of bond moments it is possible to deduce the spatial configuration of the molecules under investigation. In the case of furoin the method of vector addition has been employed for the calculation of the resultant moments for the different positions of the furyl and hydroxyl groups. For purposes of such calculations for the various structures it has been assumed that the furyl rings, the carbonyl group and the carbon atom containing the hydroxyl group lie in the same plane while the hydrogen and hydroxyl group occupy different planes (Figs. 1 A and 1 B).

Values of the moment have been obtained for configurations in which the two furyl groups oppose the primary dipole $C_1 = O_1$ at angles of 53° and 17° respectively with the OH group lying in one of the following four positions (Fig. 1 B): (*i*) in the plane containing the C_2-O_2 and the C_2-z axis but in the opposite direction to the C_2-z axis; (*ii*) along the z-axis but in the same plane; (*iii*) in the opposite direction to the x-axis coincident with the $C_1 = O_1$ direction and in the yx-plane; and (*iv*) along the x-axis and in the same xy-plane. The values thus obtained are respectively 2·16, 1·46, 3·0 and 1·76 D using for the bond moments the values C=O 2·5 D, C–O 0·86 D, H-C 0·3 D and H–O 1·53 D (Smyth[11, 12]). It may be noted that the calculated value for the third position of the OH group is fairly in agreement with the observed value of 3·24 D in benzene solution, thus indicating that the most favourable

configuration for furoin is that in which the disposition of the OH group corresponds to the $H_3 \rightarrow O$ position (see Fig. 1 B). For configurations in which the two furyl groups act in opposite directions so that their moments cancel out each other, the total moment would be the resultant of those moments of C-O, H-O, H-C and C = O bonds. In this case the moments for the four different positions of OH group works out to 2·64, 2·64, 3·9 and 1·3 D respectively, all values differing appreciably from the experimental value. If one were to assume that the furyl groups act along the direction of the primary dipole $C_1 = O_1$ at angles 17° and 53° the calculated moments for the four different positions of the hydroxyl groups turn out to be 3·6, 3·94, 5·0 and 2·51 D respectively. The fact that the experimental value corresponds to none of the above four values, rules out the possibility of existence of any of these configurations for furoin molecule. The observed moment of 3·24 D in benzene solution is the value obtained from

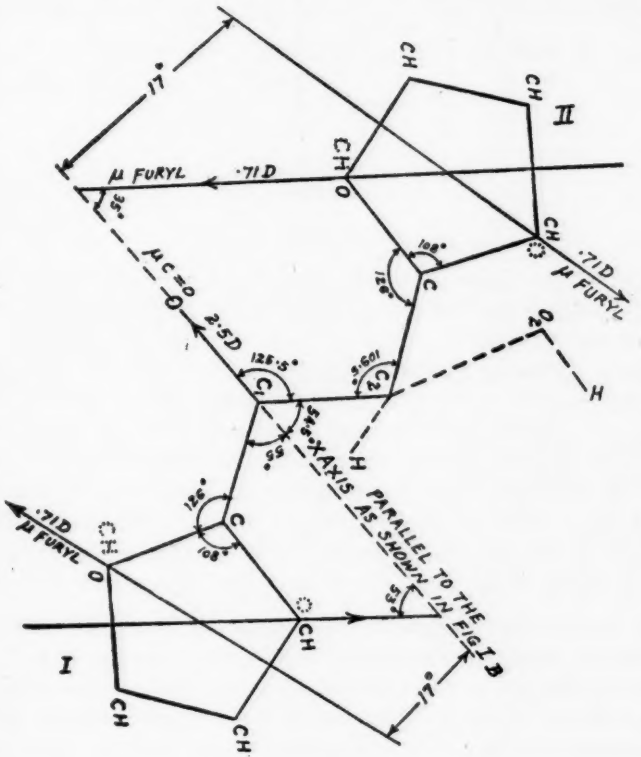

FIG. 1 A

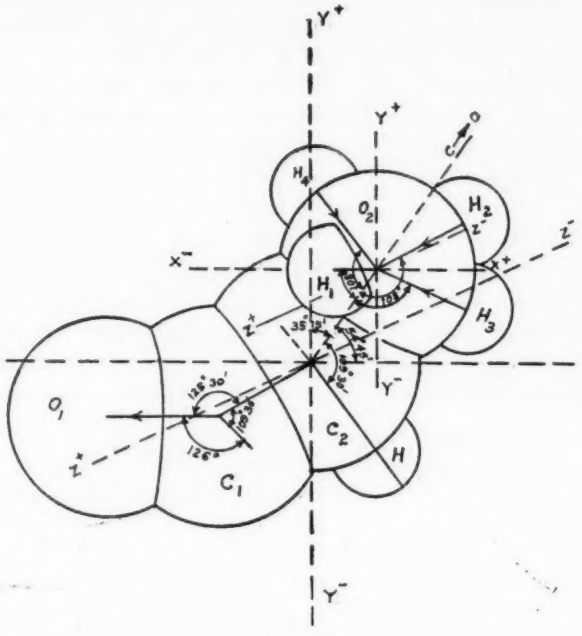

FIG. 1 B

the average of the values of Hedestrand constant α calculated from the value of 2·2570, for the dielectric constant of the solvent obtained by extrapolation of the different values of ϵ of the various concentrations to zero concentration, following Halverstadt and Kumler.[4] The fact that all values of ϵ for the various concentrations when extrapolated graphically lead to a zero value of 2·2570 for the solvent is evidence and example of abnormal solute solvent polarisation effects already discussed by Halverstadt and Kumler.[4] As mentioned earlier that configuration which gives the calculated value of 3·0 D (position $H_3 \rightarrow O$ in Fig. 1 B) and in which the OH group is quite near to the first furyl group thereby leading to the possibility of hydrogen bonding is the most favoured in the case of this molecule.

In the case of hydrofuramide, the fact that it undergoes cyclisation in liquid ammonia solution containing potassamide forming 2:4:5 trifuryl 4:5 dihydro imidazole, is itself evidence of its existence in a planar configuration. Accordingly diagrams were drawn for different possible structures of this compound taking bond angles and atomic radii appropriate to the atoms concerned from X-ray diffraction results so that the resultant moment

can be calculated for each of the configurations by the method of vector addition of moments. There is one difficulty that is encountered in such an analysis that being the magnitude of the C = N moment. In the treatment of the isocyanide bond[9] the C = N moment was assumed as two-thirds of that of the C ≡ N but such a value is too high if C = N moment contains contributions from ionic structures. A value of ·9 D twice that of the C–N bond, *i.e.*, ·45 D combined with the necessary bond values and C–H values gives calculated values in good agreement with those observed for isocyanates and iso-thiocyanates if their structures are taken as linear and this value was applied in the calculations. The C = N − C angle was given a value of 120°, this being the value found in dicyandiamide from X-ray diffraction measurements.[8] The C − C = N and C = C = C angles were taken to be 125°. The N − C − C and N − C − N angles were assumed to be 120° both taken from X-ray diffraction results for diketopiperazine, and melamine.[2, 7]

The four various configurations considered as follows are diagrammatically represented in Fig. 2.

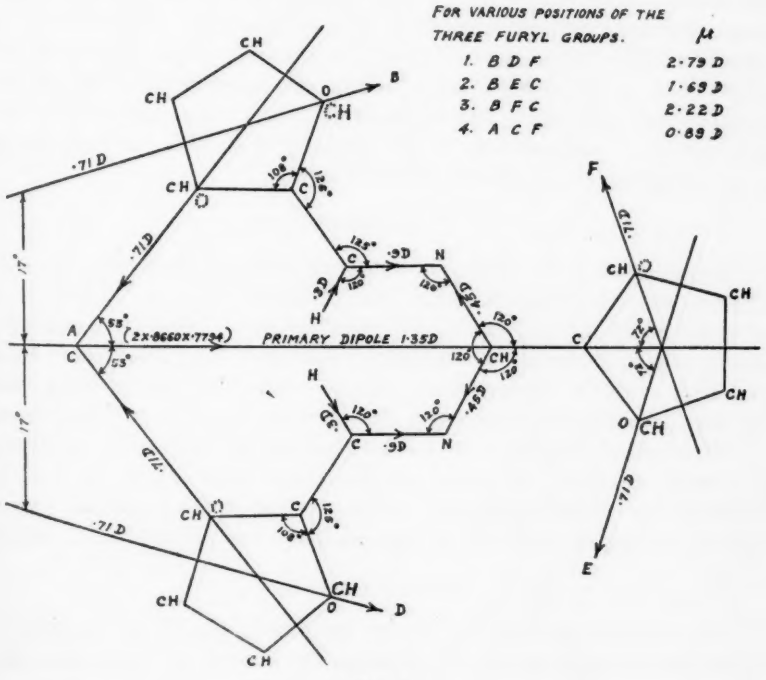

FIG. 2

1. The two symmetrically placed furyl groups on the left act along the primary at an angle of 17° with the remaining one acting at an angle of 72° to the primary either upwards or downwards.

2. One furyl group acts along the primary dipole at an angle of 17° the other acting opposite to it at an angle of 53° while the third acts opposite to it at an angle of 72° and away from the one at an angle of 17°.

3. One furyl dipole acts along the primary at an angle of 17°, the second one acting opposite to it at an angle of 53° while the third acts opposite to the primary at an angle of 72° and towards the one at an angle of 17°.

4. Both the symmetrically placed furyl groups on the left act opposite to the primary dipole at an angle of 53° while the third acts at an angle of 72° to the primary.

The values obtained for the four different configurations are respectively 2·79, 1·69, 2·22 and ·89 D. The experimental value of 2·67 D suggests that configuration 1 is most probable. In all comparisons of the type indicated here one has to reckon with theoretical and experimental limitations which preclude close agreement between calculated and experimental values. In spite of these limitations the closeness between the observed value and the calculated value for a certain configuration justifies our assignment of this particular favoured configuration to the exclusion of others. For furoin the favoured turns out to be configuration 3 (*vide* infra) (Fig. 1-B) while for hydrofuramide it is configuration 4 indicated above (Fig. 2).

SUMMARY

Measurements of dielectric constants and densities of solutions of different concentrations of furoin and hydrofuramide in benzene as also refractive index measurements for hydrofuramide, have been carried out and the dipole moments of the above substances calculated from values of 'P' arrived at by the application of the Hedestrand's method of extrapolation. The values of dipole moments of the two substances are: Hydrofuramide $= 2 \cdot 66 \pm \cdot 01$ D. Furoin 3·24 D. The structures of furoin and hydrofuramide have been discussed from the experimentally obtained values and those calculated for various positions of furyl groups in the latter and furyl and hydroxyl groups in the former by the method of vector addition of moments.

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EXPERIMENTAL INVESTIGATION OF NOISE ASSOCIATED WITH MODULATED PULSES

By V. Narayana Rao, M.Sc. (Tech.) (Manchester)

(*Department of Electrical Communication Engineering, Indian Institute of Science, Bangalore*)

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Introduction

The investigation of the nature of the noise associated with modulated pulses is very important in determining the merit of a pulse communication system from the point of view of the signal to noise ratio. If we ignore the external sources of noise which are quite negligible at the carrier frequency in use, the noise in a pulse communication system originates mainly in the early stages of the receiver. The r.f. pulse signal on reaching the receiver input, is amplified and then converted by means of the local oscillator to an intermediate frequency signal. It is then amplified to a suitable level and detected by a diode detector. The fluctuation noise produced in the input circuit and the r.f. amplifier and converter tubes, also undergoes the same series of processes as the signal, as shown in Fig. 1. The noise voltage

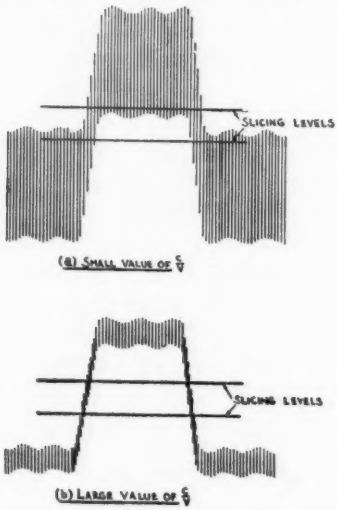

Fig. 1

appears between the pulses (known as " the free noise "), on the top of the pulses (known as " the modulating noise "), and also on the edges of the pulses (known as " the edge noise "). In pulse phase, frequency and width modulation systems, as the intelligence is solely determined by the position of the leading and trailing edges of the pulse, it is clear that under usual circumstances, the pulses can be chopped off both at the top and the bottom and hence the free and modulating noises can be eliminated, without in any manner affecting the modulation content. This process is known as " slicing " and it improves the signal to noise ratio considerably. Evidently, this process cannot be applied to the case of amplitude modulated pulses and here the free noise can be got rid of by means of a synchronised pulse gate.

Theoretical Analysis

The noise voltage appearing at the input of the detector can be considered to consist of a number of sinusoidal components whose amplitudes are distributed according to the overall frequency response of the receiver and whose phases are related to one another in a completely random manner. If the bandwidth of the overall response is small compared to the carrier frequency ω_0, the noise voltage can be represented by,

$$v = [a(t) + jb(t)]\, e^{j\omega_0 t} \tag{1}$$

Here a and b are slowly varying functions of time and if they are represented as $Ae^{\alpha t}$ and $Be^{\beta t}$, then the coefficients α and β will be very small compared to ω_0. Also it can be shown that a and b follow the Gaussian probability distribution given by

$$p_1(x) = \frac{1}{V\sqrt{2\pi}}\, e^{-x^2/2V^2} \tag{2}$$

where V is the r.m.s. value of x.

The noise accompanying a signal pulse is the superposed effect of the noise of the above type together with the sinusoidal voltage of the intermediate frequency having the pulse as its envelope. Just prior to detection, the free noise, the edge noise and the modulating noise will all follow the same probability distribution which, however, they cease to follow after detection. The detection process will impose the restriction on the free noise that its value should always be positive and the resulting probability distribution will be

$$p_2(x) = \frac{\dot{x}}{V^2}\, e^{-x^2/2V^2}, \tag{3}$$

where $p_2(x)\,dx$ represents the probability of finding the noise voltage, at any moment, between the values of x and $x + dx$ and V represents the

r.m.s. value of the noise amplitude. This is the well-known Rayleigh distribution.

The modulating noise is characterised by the fact that it is composed of noise superposed on a steady carrier $Ce^{j\omega_0 t}$ just prior to detection. The process of detection will impose the restriction that the value of C *plus* the noise voltage should always be positive. It has been shown[5] that if the carrier amplitude C is much greater than the r.m.s. noise voltage V, the modulating noise will then follow the Gaussian distribution about a mean value of C. Thus, the probability of finding the noise voltage between the values y and $y + dy$, where y is the voltage measured from the level C (*i.e.*, $y = C - x$), is given by

$$p_3(y) = \frac{1}{V\sqrt{2\pi}} e^{-y^2/2V^2} \tag{4}$$

As regards the edge noise, its effect is quite small as it occurs for short durations of time corresponding to the leading and trailing edges of the pulse wave-form. Its probability distribution is similar to that of the modulating noise.

From a knowledge of the two distribution laws, equations 3 and 4, the distribution of noise voltage from the top to the bottom of the detected pulse can be determined. Before proceeding further, it will be convenient to reduce the equations 3 and 4 to more convenient forms. If the quantities x, the voltage measured from zero level, and V, the r.m.s. value of noise voltage, are expressed as fractions of C, the carrier amplitude, then equation 3 becomes

$$p_2'\left(\frac{x}{C}\right) = \frac{Cx}{V^2} e^{-x^2/2V^2} \tag{5}$$

Similarly if y and V are expressed as fractions of C the equation 4 becomes

$$p_3''\left(\frac{y}{C}\right) = \frac{C}{V\sqrt{2\pi}} e^{-y^2/V^2} \tag{6}$$

On expressing y as $C - x$, equation 6 can be written as,

$$p_3'\left(\frac{x}{C}\right) = p_3''\left[\left(1 - \frac{x}{C}\right) = \frac{C}{V\sqrt{2\pi}} e^{-(C-x)^2/2V^2}\right. \tag{7}$$

The modified probability function $p_2'(x/C)\, d(x/C)$ represents the probability of finding, at any instance, the free noise voltage in the range x/C to $(x + dx)/C$ and similarly $p_3'(x/C)\, d(x/C)$ represents the probability of finding the modulating noise in the range x/C and $(x + dx)/C$. Fig. 3 shows these results in a graphical form for two different values of the parameter C/V. It is seen, from these curves, that the probability functions

have two maxima one at $x/C = V/C$ and another at $x/C = 1$. Also, the higher the value of C/V, the narrower is the spread of each of these curves.

As mentioned in the introductory remarks, one of the most distinguishing features of pulse communication is that the noise can be minimised by the process of slicing. Suppose a thin slice is cut from the pulse as shown in Fig. 1 *b*. Then the amount of free and modulating noises accompanying this sliced pulse depends directly on the value of the probability functions $p_2'(x/C)$ and $p_3'(x/C)$. Thus referring to Fig. 3, if $C/V = 10$, then at slicing level $x/C = 0{\cdot}1$, the free noise is a maximum and the modulating noise is insignificant and similarly at $x/C = 1$, the modulating noise is a maximum, the free noise being negligible. At points, in between, the free and modulating noise contributions have intermediate values as shown by the probability distribution curves. Therefore the values of the probability functions may be regarded as a measure of the noise accompanying sliced pulse for different slicing levels. It is important to note here, that the edge noise has not been taken into consideration as the pulse is assumed to have steep leading and trailing edges.

It is clear from an examination of the probability distribution curves of Fig. 3, that when the signal to noise ratio (S/N) is high, the slicing level can be anywhere near the middle of the pulse height. However, if the S/N ratio is small the choice of the slicing level is important in determining the S/N ratio of the sliced output. The amount of noise accompanying the sliced pulse will be proportional to

$$(1 - M)\int_{S/C}^{(S+\Delta S)/C} p_2'(x/C)\, d(x/C) + M\int_{S/C}^{(S+\Delta S)/C} p_3'(x/C)\, d(x/C) = N \qquad (8)$$

where S is the slicing level, ΔS is the thickness of the sliced pulse and M is the duty factor of the pulses. The optimum slicing level is that for which N is a minimum and hence it can be determined by setting $dN/dS = 0$ and evaluating S. Also it is important to note that if the value of C/V is small a more accurate expression[1] for $p_3'(x/C)$, given by equation 9, should be used

$$p_3'(x/C) = \frac{(C - x)\,C}{V^2}\, e^{-[C^2+(C-x)^2]/2V^2}\, I_0\left(\frac{[C - x]\,C}{V^2}\right) \qquad (9)$$

where I_0 is the modified Bessel function of the first kind and of zero order.

The determination of the optimum slicing level from equation (8) is difficult. Following a simpler method, due to Jelonek,[5] ΔS is assumed to be sufficiently large so that the free noise can be neglected above the level

$S + \Delta S$ and the modulating noise below the level S. The formula for the optimum slicing level will be then given[5] by

$$S_{opt} = C\left\{\frac{1}{2} + \frac{\log_e\left[\sqrt{\pi}\,\frac{C}{V}\left(\frac{1}{M} - 1\right)\right]}{\left(\frac{C}{V}\right)^2 - 1}\right\} \tag{10}$$

EXPERIMENTAL VERIFICATION

An experimental investigation of the noise distribution with height of detected pulses and a study of the correlation between the noise distribution and probability functions is important for verifying the above theory. The experimental arrangement, shown in Fig. 2, was set up for this purpose. In this arrangement the r.f. pulse signal obtained at the output of a generator is applied, at a low level, to a wide-band r.f. amplifier and after amplification, is detected and applied to a video amplifier. The output of this will consist of the pulse signal mixed with noise and is applied to a slicing circuit followed by a device for measuring the noise power. A brief description of the different parts of Fig. 2 will now be given.

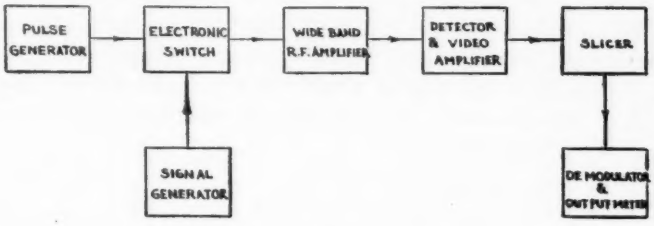

FIG. 2

The pulse modulator used was of the type described in reference (6) and this was set to produce pulses of repetition frequency 10,000 cycles per sec. and of duration approximately 4 microseconds. An electronic switching device was used for producing the r.f. pulses. Full details of this device will be found in reference (3). The wide band r.f. amplifier was a radar i.f. amplifier having a midband frequency of 14 mc/s and a band width of ± 1 mc/s. With this bandwidth, pulses of 2 microsecond duration and above could be properly reproduced.

The slicing circuit formed an important part of the set up. The output from the video amplifier was applied to a cathode follower circuit, the output of which was capacitatively coupled to the control grid of a pentode having sharp cut-off characteristics. The cathode of this tube was held

at an adjustable positive potential and a voltmeter was connected to measure this voltage. The screen and plate of the pentode were held at a positive potential of about 12 volts relative to the cathode and thus the grid base of the tube was kept quite low. A diode was connected between the control grid and ground in order to ensure that the pulse voltage applied to the pentode started always from a constant level, namely, zero volts. A suitable load resistance, of the order of 3,000 ohms, formed the anode load of the pentode. The amplitude of the applied pulse was kept at, approximately, 20 volts and by properly adjusting the cathode potential, the pulse could be sliced at any desired level. The sliced pluse was then amplified and after being filtered by means of a low pass filter, was applied to a cathode follower stage. A thermo-couple instrument connected as the cathode load served to measure the noise and the signal powers.

The experimental procedure adopted was briefly as follows:—The duty factor of the pulses was adjusted to the desired value. Then the ratio of the pulse height to the r.m.s. noise voltage, C/V, was set to the desired value. For each value of C/V, the pulse was sliced at different levels and the noise

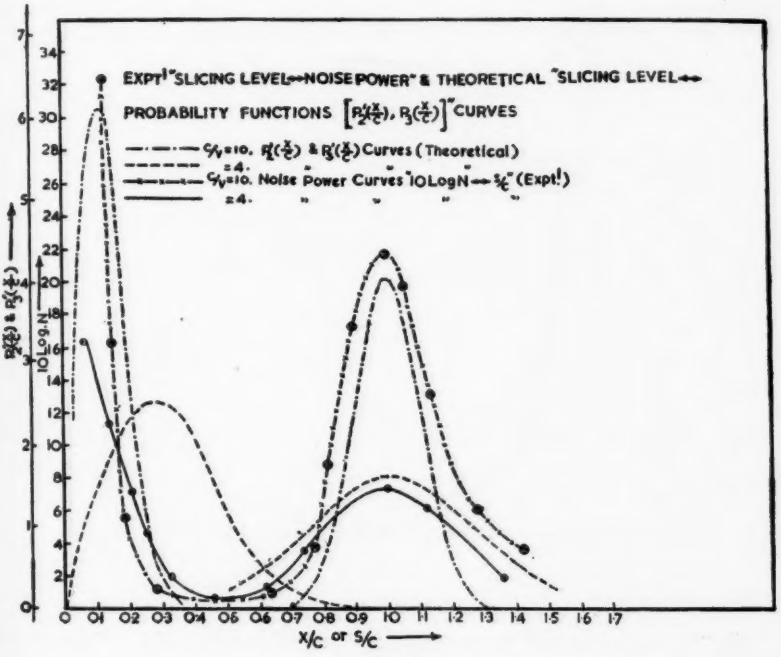
EXPT^L "SLICING LEVEL↔NOISE POWER" & THEORETICAL "SLICING LEVEL↔
PROBABILITY FUNCTIONS [R'2(X/C), R'3(X/C)]" CURVES
C/V=10. R'2(X/C) & R'3(X/C) Curves (Theoretical)
=4. " " " "
C/V=10. Noise Power Curves "10LogN↔S/C" (Expt^L)
=4. " " " "
R'2(X/C) & R'3(X/C)
10LogN
X/C or S/C
0 01 02 03 04 06 06 07 08 09 10 11 12 13 14 15 16 17

FIG. 3

power in the output was measured for each of the slicing levels. Also the pulse was width-modulated by a sinusoidal wave to a certain depth and the output power was measured with and without modulation. Thus the signal to noise ratio was determined for various slicing levels.

EXPERIMENTAL RESULTS

(*a*) Pulses having a duty factor of 1/15 were generated. The noise voltage was adjusted to provide C/V ratios of 10 and 4 respectively. The pulses were then sliced at different heights and the logarithm of the noise power (N) was plotted as a function of S/C (see Fig. 3). The probability distribution curves have also been plotted on the same graph.

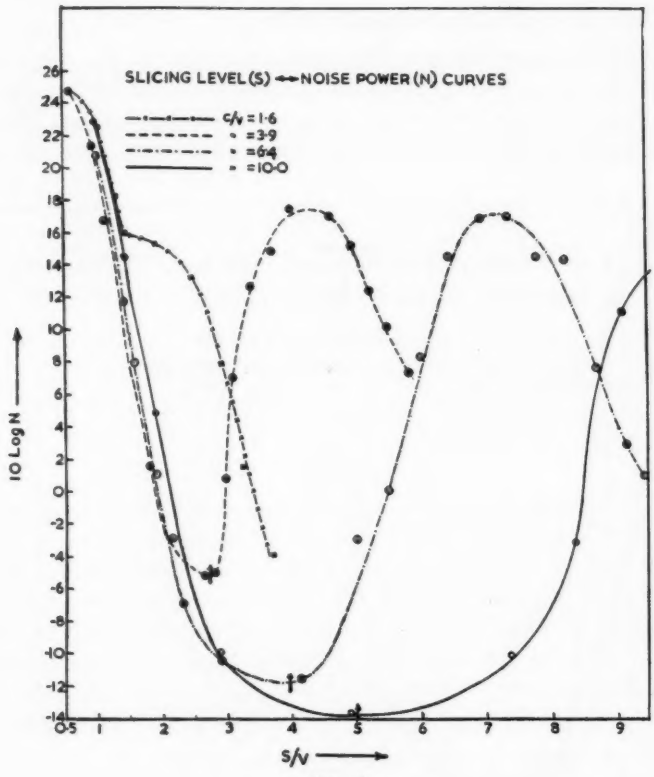

FIG. 4

(*b*) The duty cycle of the pulses was changed over to 1/25. This change-over was for the purpose of studying the noise distribution under different

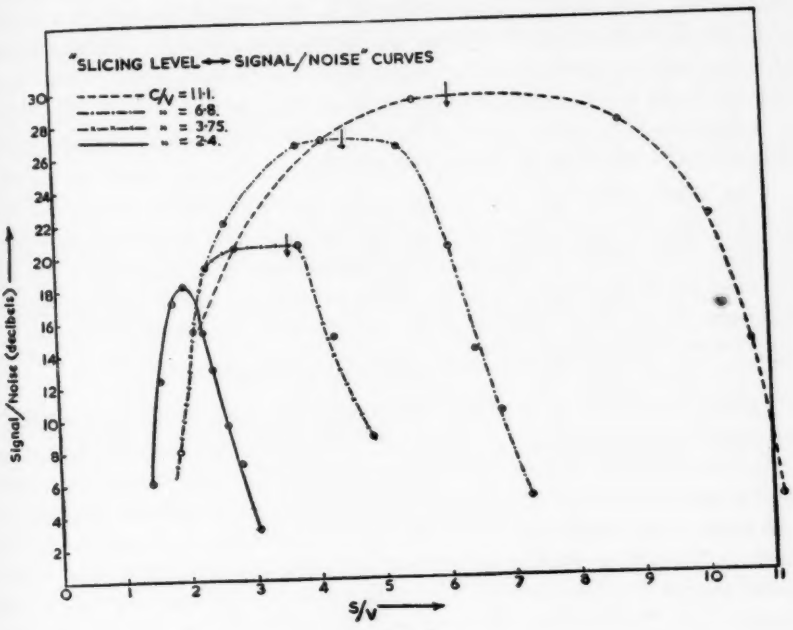
"SLICING LEVEL ↔ SIGNAL/NOISE" CURVES
C/V = 11·1.
" = 6·8.
" = 3·75.
" = 2·4.
Signal/Noise (decibels)
S/V

FIG. 5

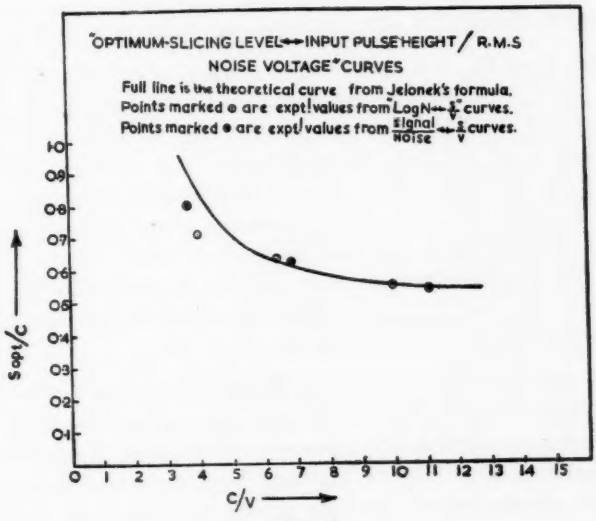
"OPTIMUM-SLICING LEVEL ↔ INPUT PULSE HEIGHT / R.M.S NOISE VOLTAGE" CURVES
Full line is the theoretical curve from Jelonek's formula.
Points marked o are expt! values from "LogN ↔ S/V" curves.
Points marked • are expt! values from "Signal/Noise ↔ S/V" curves.
Sopt/C
C/V

FIG. 6

conditions. The pulse to noise ratio, C/V, was set at the values 1·6, 3·9, 6·4 and 10·0 and for each setting the pulses were sliced at different heights and the measured noise power was plotted as a function of S/V (see Fig. 4). The optimum slicing levels were deduced from Fig. 4 and these are plotted as a function of C/V in Fig. 6. The values obtained from Jelonek's formula (equation 10) are also shown in this figure.

(*c*) With pulses of duty factor 1/25, and with values of C/V = 2·4, 3·8, 6·8 and 11·1 the pulses were modulated by a 1000 cycle tone to a depth of 10%. The signal to noise ratio was determined as a function of the slicing level for each setting of C/V. These results are shown in Fig. 5. The optimum slicing levels deduced from these results are shown in Fig. 6.

DISCUSSION OF RESULTS AND CONCLUSION

Referring to Fig. 3, it is seen that the experimental ' noise power—S/C ' curves for the values of C/V = 10 and 4, agree fairly well with the theoretical probability function curves. Both the experimental and theoretical curves have a maximum value at $x/C = 1$ and they are symmetrically disposed on both sides of the maximum. They both have a minimum value at $x/C = 0{\cdot}5$. There is, however, a certain discrepancy between the theoretical and experimental curves for low value of C/V. This can be explained by taking into consideration the fact that the practical slicing thickness is finite and also that the edge noise cannot be neglected in practice. Making due allowance for these factors it can be concluded that the experimental results confirm the theoretical deductions obtained for the noise distribution.

It is seen from Fig. 4 that the output noise power diminishes considerably as the slicing level is moved from zero level to the optimum level. Thus with a value of C/V = 10, the reduction in noise power is about 37 decibels. Also it is seen that for pulses with large values of C/V, the variation in noise power near the level S/C = 0·5, is quite small and as the value of C/V diminishes, the location of minimum noise power point becomes quite critical. The results obtained from " Signal/Noise ratio—S/V " curves are in agreement with the results obtained from " noise power-slicing level " curves. And hence it may be concluded that the condition for minimum noise power also ensures maximum signal to noise ratio.

Finally, the experimental optimum slicing level values for different values of C/V are seen to agree fairly well with the values given by Jelonek's formula (see Fig. 6). For small values of C/V, however, the theoretical values are somewhat higher as may be expected from the simplifying assumptions made in the derivation of optimum slicing level formula.

Summary

The theory of noise associated with pulses is considered from the point of view of application to the study of noise in pulse communication. The process of slicing and its effect on the signal to noise ratio are also considered. Experimental arrangement to verify the theoretical deductions and also the optimum slicing level formula are given. The results are fully discussed.

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SOME REGULARITIES IN THE MASSES OF HEAVY PARTICLES

By Kantilal M. Gatha
(*M. G. Science Institute, Ahmedabad*)

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I. Introduction

In recent years, a number of heavy particles have been discovered. While most of them are known as mesons, some are called V-particles because of the nature of their decay tracks. In the present investigation all these as well as nucleons will be called heavy particles. These particles are usually characterised by their charge and spin quantum numbers as well as their rest masses. These masses have been determined with some accuracy in the case of a few particles only. Various attempts, notably by Born[1] and Darling,[2] have been made to account for the magnitudes of these masses by means of theories based upon certain assumed fundamental principles. However, no acceptable correlation of their theoretical mass spectra with the observed masses has so far been obtained. It is well known that in the development of the quantum theory of atomic spectra several empirical formulations had preceded their complete theoretical explanation. Following this clue several attempts, for example by Fürth[3] and Freeman,[4] have been made to obtain suitable empirical rules for the rest masses of these particles. However, since only a few masses have been measured with sufficient accuracy, it appears rather premature to formulate such complicated rules as proposed by them. On the other hand, one may hope to obtain a valid empirical rule provided the correct law for these masses either has a simple form or can be approximated to the same. Such a simple rule is proposed in the present investigation.

II. The Proposed Empirical Rule

Since the validity of an empirical rule can be tested solely by its ability to represent the experimental data, it is not necessary to give here the detailed procedure of its development. Hence, the proposed rule is presented directly as follows:—

$$M_n \simeq n\bar{M} \qquad (1)$$

where, M_n=the rest mass of the particle designated by the integral quantum number n,

$\bar{M}$ = the mass quantum for heavy particles.*

On the basis of numerical and dimensional similarity, it is further suggested that

$$\bar{M} = m/2\alpha \qquad (2)$$

where, m = the electron mass,

$\alpha = e^2/\hbar c$ = the fine structure constant.

III. Comparison with the Experimental Observations

In Table I have been listed the various heavy particles to which the above rule has been applied. The decay schemes given therein are those that have been assumed while determining the observed masses. The statistics have been obtained on the basis of their assumed conservation during the process of decay. Firm or tentative values of the mass quantum number n have been assigned to the various particles and the corresponding mass values M_n have been calculated on the basis of the proposed empirical rule using $1/\alpha = 137{\cdot}03$[5] but neglecting the probable error on the same. The latest values of the observed masses M_{ob}, together with their probable errors, are also given for comparison. The deviations of the observed masses from the corresponding calculated masses are also shown. However, of greater interest are the ratios M of the observed masses to their corresponding quantum numbers. Lastly, the deviations of M from the proposed mass quantum $\bar{M} = m/2\alpha$ have been calculated. All masses have been tabulated in the electronic mass units.

IV. Discussion of the Tabulated Results

(1) *Deviations.*—Though one may regard the deviations of the observed masses M_{ob} from the corresponding calculated masses M_n as small compared to the proposed mass quantum $\bar{M}$, they cannot be regarded as very small compared to the same except for small quantum numbers. They appear to be somewhat magnified at large quantum numbers. However, the ratio M_{ob}/n is nearly constant for all quantum numbers. This is consistent with the proposed existence of a mass quantum. Moreover, the deviations of M from the proposed mass quantum $\bar{M}$ are very small compared to $\bar{M}$ and are distributed on both sides of the same. Thus they can

* Freeman[4] has also mentioned the possibility of the existence of such a mass quantum without, however, following it through.

TABLE I

Particles	Decay Products	Statistics	n	$M_n = n\bar{M}$	M_{ob}	$(M_{ob} - M_n)$	$M = M_{ob}/n$	$(M - \bar{M})$
$\mu\pm$-meson ..	$e\pm + 2\nu$	Fermi	3	205·5	$209·6 \pm 2·4$[6]	$+(4·1 \pm 2·4)$	$69·9 \pm 0·8$	$+(1·4 \pm 0·8)$
$\pi\pm$-meson ..	$\mu\pm + \nu$	Bose	4	274·1	$276·1 \pm 2·3$[6]	$+(2·0 \pm 2·3)$	$69·0 \pm 0·6$	$+(0·5 \pm 0·6)$
π^0-meson ..	2γ	Bose	4	274·1	$265·5 \pm 3·1$[6]	$-(8·6 \pm 3·1)$	$66·4 \pm 0·8$	$-(2·1 \pm 0·8)$
$\xi\pm$-meson ..	$\pi\pm + \pi^0$	Bose	(8)	(548·1)	535 ± 35[7]	..	..	..
ξ^0-meson ..	$\pi^+ + \pi^-$	Bose	8	548·1	556 ± 4[7]	$+ (8 \pm 4)$	$69·5 \pm 0·5$	$+(1·0 \pm 0·5)$
V_2^0-particle ..	$\pi^+ + \pi^-$	Bose	(12)	(822·2)	779 ± 27[8]	..	..	..
$\tau^\pm$-meson ..	$\pi\pm + \pi^+ + \pi^-$	Bose	14	959·2	973 ± 6[9]	$+(14 \pm 6)$	$69·5 \pm 0·4$	$+(1·0 \pm 0·5)$
τ^0-meson ..	$\pi^+ + \pi^- + \pi^0$	Bose	(14)	(959·2)	900 ± 100[7]	..	..	..
K±-meson ..	$\pi\pm + \xi\mp$	Fermi	(15)	(1027·7)	1080 ± 100[7]	..	..	..
	$\mu\pm + 2\nu$	Fermi	(17)	(1164·8)				
	$\mu\pm + \nu + \pi^0$	Bose	(16)	(1096·2)	1480 ± 100[7]	..	..	..
	$\mu\pm + \nu + 2\pi^0$	Bose	(20)	(1370·3)				
$\chi\pm$-meson	$\pi\pm + \tau^0$	Bose	(22)	(1507·3)				
Proton	..	Fermi	27	1849·9	1836·5	$-(13·4)$	68·0	$-(0·5)$
Neutron	$P + e^- + \nu$	Fermi	27	1849·9	1838	$-(11·9)$	68·1	$-(0·4)$
V_1^0-particle	$P + \pi^-$	Fermi	32(?)	2192·5	2187 ± 5[10]	..	..	..
			33	2261·0	2260[7]			
	$P + \pi^- + \nu(?)$	Bose	(?)	(?)	(?)			

be regarded as some higher order corrections on $\bar{M}$. This makes the hypothesis of representing the mass quantum by $\bar{M}$ admissible.

(2) *Statistical Property.*—It may be noted that the proposed mass quantum numbers n are analogous to the nuclear mass numbers A. However, the latter possess the statistical property by virtue of which the odd and the even values of A denote the Fermi and the Bose statistics respectively. In the present case also one observes that the quantum numbers n possess the same statistical property. This lends further interest to the proposed scheme. The only exception to this otherwise general statistical property of the quantum numbers n appears in the case of one of the mass values for the V_1^0-particle which, for Fermi statistics, requires the even quantum number $n = 32$. However, Brueckner and Thompson[11] have shown that the various tests, usually employed to establish the assumed two particle decay, are not sensitive enough to exclude the presence of a light neutral particle among the products of decay. Thus it seems that neither the statistics nor the mass values for the V_1°-particle are so far determinate enough to provide a clear exception to the statistical property of the proposed mass quantum numbers. It is, therefore, on the basis of this property that tentative quantum numbers have been assigned to the $\xi^\pm$-meson, the V_2°-particle, the τ°-meson, the $K^\pm$-meson and the $\chi^\pm$-meson. The quantum number $n = 14$ is assigned to the τ°-meson considering it to be the neutral analogue of the $\tau^\pm$-meson. It may further be noted that this statistical property raises the mass interval, for a particular statistics, from $\bar{M} = m/2\alpha$ to $2\bar{M} = m/\alpha$. This makes the deviations of M_{ob} from the corresponding M_n appear smaller when compared to the new mass interval m/α.

(3) *General Remarks.*—It should be noted here that the classification of nucleons along with highly unstable particles is somewhat problematical. Moreover, one may presumably assign the quantum number $n = 0$ to the light particles like the neutrino, the electron and the photon, treating any small rest masses as higher order corrections. The problem of the missing quantum numbers in the proposed scheme is a matter for future investigation.

V. An Alternative Expression for the Proposed Rule

Since the various particle masses can be derived on the basis of purely electrodynamic constants m and α, electrodynamics seems to play a fundamental role in nature. However, one can regard the combination $m/2\alpha$, rather than m and α separately, as of greater significance. Now $m/2\alpha$ can

also be expressed as $\hbar/2ac$, where $a = e^2/mc^2$ is the classical electron radius. One can consider 'a' as a quantum of length and rewrite the proposed rule in its terms as follows:—

$$M_n \simeq n\hbar/2ac. \tag{3}$$

VI. CONCLUSION

One can conclude that the proposed empirical rule $M_n = n\overline{M}$, is consistent with the experimental observations. The mass quantum $\overline{M}$ can be identified with $m/2a$. Further, the mass quantum numbers n possess the same statistical property as exhibited by the nuclear mass numbers A. It would, therefore, be interesting to test further the validity of this rule as more particle masses are measured with a greater accuracy.

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